BONE FIXATION AND THE CORROSION RESISTANCE OF STAINLESS STEELS TO THE FLUIDS OF THE HUMAN BODY[1]

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ABSTRACT

Bone fixation plates and screws were prepared from three different stainless steels and from one chromium-cobalt alloy. These were tested under the most carefully controlled conditions, closely duplicating the conditions prevailing in the normal human body. The following media were included: physiological salt solutions; plain serum; serum saturated with an excess of sulfanilamide; serum inoculated with staphylococcus aureus; and serum acidified to pH 5.0 to 5.5 by the addition of potassium acid phosphate. Results showed that stainless steel, such as AISI Type 302, was the most corrosion resistant.

INTRODUCTION

The research covered in part by this report was assigned to Dr. Clay Ray Murray[3] and Colin G. Fink by the Orthopedic Committee of the National Research Council, Washington, D. C. in December 1941. The research was rated as "Class A" meaning that the funds required for carrying out the research were in the first group to be allocated.

Specifically, we were instructed to find as soon as possible the most acceptable metal or alloy available for bone fixation and determine its chemical and mechanical properties. Included in the mechanical properties were to be studies of the effect of straining the plates in the mechanical testing laboratory as well as in vivo under functional strain with various techniques of fixation.

By bone fixation is meant the bridging of the bone fracture with a narrow metal plate, from 3 to 6 inches (7.5 to 15 cm.) in length, which is fixed by several screws driven into the uninjured sections of the bone above and below the fracture.

In order to better appreciate the fact that the fluids of the human body will attack nearly every known metal, we cite a few of the body acids that have been definitely isolated: uric, lactic, hydrochloric, oxalic, phosphoric, butyric, ascorbic, gluconic, acetic and other fatty acids, amino acids, etc.

It is well known that the various fluids present in the human body are of complex and constantly varying nature. The change in acidity (or pH)

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[3] To our deep sorrow and regret, Dr. Murray died on June 14, 1947, before this report was completed.

is at times pronounced and has been frequently determined. In striking distinction from ordinary corrosion testing, the metal or alloy for bone fixation is tested in body fluids protected against the atmosphere.

In the selection of metals acceptable for the fixation of fractured bones, we are confronted with a relatively complex problem. Basing our selection of this or that metal on the results of salt spray tests is not acceptable on various counts. In general, the ideal corrosion test is the test that reproduces actual "service conditions." In the case of bone fractures "actual service conditions" implies the several chemical and electrochemical reactions and reaction products involved during the healing of the fracture as well. According to Clay Ray Murray (1) there occurs immediately following fracture, death of tissue and hemorrhage in both soft parts and hard parts of the bone as result of trauma. Then, within the next few hours occurs the reaction of inflammation, secondary to the autolytic products of tissue death and hemorrhage into the tissues. Then occurs a markedly lowered pH in the local tissue fluids due to the products of tissue-death and hemorrhage, until such time as the local minute circulation can disperse them. Next follows the formation of a fibrin network by the clotting of hemorrhage and exudate.

As the healing progresses the pH rises to a point which allows only minimal phosphatase activity, a slow calcium deposition occurs, but ceases as a local healing process when tissue differentiation is complete. The final pH after healing is 7.35 as against 5.3 to 5.6 immediately following trauma.

During the many years that bone fixation of fractures has been practiced, little or no attention was placed on the chemical and electrochemical reactions involved, notably those reactions taking place at the point of fracture immediately following trauma; and those reactions taking place during and after the healing process. This lack of attention to the chemical and electrochemical attack of the various metals used in the past is the more surprising in view of the fact that all metals, with very few exceptions, interact with the bone or with the fluids in contact with the bone, giving rise to readily detectable and usually characteristic discoloration of the bone and/or disintegration of bone structure immediately traceable to the presence of this or that particular metal.

A wide variety of metals has been tried including silver, gold, lead, tin, aluminum, copper, iron, steel, nickel, bronze, nickel silver, etc. The long and unhappy history of metals in surgery has been a consistent record of necrosis of bone and soft tissues, interference with bone growth and repair, and delayed union, mal-union, and non-union of bone. At the close of the last century surgeons in England were using carbon steel and nickel-silver strips (2). Neither of these metals proved satisfactory. After a few weeks following the operation, plates of either carbon steel or nickel silver were "rejected" by the bone with the accompaniment of much local swelling, pain, tenderness, and discolored sterile pus.

The reaction of inflammation is accompanied by a lowering of the pH of the local tissue fluids. As long as the bone is exposed to these fluids of markedly low pH, decalcification of the bone takes place.

Any metal selected for bone fixation must be resistant to attack at the relatively low pH of the local tissue fluids which prevail during the first hours after surgical operation. Furthermore, the metal brace must be

resistant to attack by the body fluids in contact with the bone and with the metal brace during the days and months that follow the operation. The metal strip may remain in the body or the surgeon may decide to remove the strip after a certain time for healing the fracture has elapsed.

TEST PROCEDURE

Each specimen before sealing into the glass tube was cleaned thoroughly with a brush and soap to remove packing particles, etc. After rinsing in distilled water and drying, each piece was degreased in toluene vapor (laboratory vapor degreaser). The metal piece was then gently swirled for one minute in hot dilute NaOH solution. It was thoroughly rinsed in hot distilled water and dried.

Each piece was weighed to the nearest tenth of a milligram. After weighing, each specimen was wound with non-absorbable cat gut at each end. Where galvanic action was studied the screws were securely tied to one end of a plate with cat gut. Just before placing a metal specimen into its tube, it was placed in vigorously boiling water for a time long enough to sterilize it.

The glass tubes employed were made of soft glass test tubes 1 in. x 8 in. (2.5 x 20 cm.) and $\frac{3}{4}$ in. x 6 in. (1.8 x 15 cm.) according to size of metal test piece. Three dimples were made in the side of each tube, $\frac{3}{4}$ in. (1.8 cm.) from the bottom to support a $\frac{3}{16}$ in. (5 cm.) thick cork disk on which the end of the metal plate would rest. This guarded against breakage of the tube during loading and testing.

Best quality corks were steeped in water for a day, and then gently boiled in frequent changes of water to extract soluble matter. They were then slowly dried at low temperature. When dry they were placed in molten paraffin for 1 hour to impregnate them. The cork disks which served as bottom supports for the plates were treated likewise.

The various corrodants were prepared at the College of Physicians and Surgeons, New York City, under sterile conditions as usually practiced there. The test tubes were sterilized by boiling; and while hot, the cork disk, taken from the smoking hot paraffin bath with sterile forceps, was pushed to its proper place. This procedure, as well as subsequent ones, was done in a sterile cabinet irradiated by ultra-violet light. The metal plate was inserted next, followed by a measured dose of corrodant from a syringe. Immediately thereafter, a cork stopper taken from the smoking hot paraffin bath was pushed home to seal the tube. Linen cord was tied over the stopper to insure that it stayed in place. As the top of the tube cooled, a little paraffin was painted over the glass-cork junction. After the assembly was completely cooled, the cork end of the tube was quickly dipped into a 50-50 mixture of beeswax and rosin, held at just above its melting point. The tubes were assembled in the test rack which operated in a thermostat held at 37°C. $\pm$ 0.01°C. All operations on the plates and tubes before sealing were done while using sterilized rubber gloves.

The test rack (Fig. 1) was essentially a bronze frame capable of holding 25 loaded glass tubes in an upright position, while the whole assembly was submerged in the thermostat. The test rack was mounted so that it could be slowly and constantly moved to a tilted position to such an angle, as determined by test, that the metal specimens would tumble from their

former position to a new one against the side of the tube. Then the rack would be tilted in the opposite direction until the specimens again tumbled. One complete cycle required about 30 seconds. The agitation occurred as the specimen moved relative to the corrodant. The motion was small but it is believed to have been sufficient to prevent static conditions. The role of the cat gut winding on each end is apparent after considering this activity.

The thermostat water was sterilized continuously with silver (oligodynamic method) purely as a matter of precaution.

At the completion of the tests each tube was unsealed and the specimen removed. The specimens were scrubbed clean with a brush under running water. They were then treated with boiling distilled water and dried, then weighed. However, to be certain of the cleaning operations, the specimens were treated in hot dilute NaOH solution as at the beginning. No changes

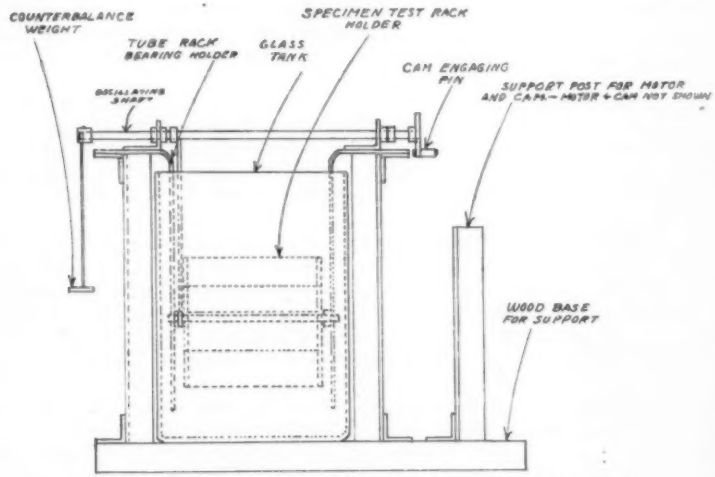

FIG. 1. Sketch of bone plate test equipment (not to scale)

in weight were noted when the weights were compared with those taken after scrubbing only.

Surface areas of plates were calculated from accurately made measurements. In the case of the screws, attempts to obtain area by using the Langmuir monomolecular film technic were not successful. Two methods finally evolved. In the first, a screw was sectioned longitudinally, after measurements of its dimensions were made with calipers. The thread profile was projected by means of a camera lucida from a microscope. The enlarged profile was traced and measured. Knowing the magnification factor enabled a fairly good approximation of the area to be made.

The second method involved the electrodeposition of nickel. The screw was sectioned and the mean thickness of the deposit was determined from numerous readings. Knowing the density of nickel, the increase in weight and the mean thickness of the nickel enabled the estimation of area. This method was successfully applied to the plates as well.

EXPERIMENTAL

The following corrodants (Table I) were used in our tests on metal samples both as received as well as on strained metal samples:

Corrodants

1. Physiological salt solution (PS)
2. Plain serum (S)
3. Serum saturated with an excess of sulfanilamide (SF)
4. Serum inoculated with staphylococcus aureus[4] (SSA)
5. Serum acidified to pH 5.0 – 5.5 with KH_2PO_4 (SA)

TABLE I. *Two sets of plates* (a *and* b) *as received from manufacturers*

Weight changes in mg./dm.²/day; duration of each test—6 weeks; body temperature

Corrodant	Vitallium		Type 316-A		Type 316-B		Type 302	
Run	a	b	a	b	a	b	a	b
PS	−0.1	0.1	−0.2	0.1	0.0	0.0	+0.2	+
S	−0.5	0.2	0.0	0.0	0.0	0.0	−0.0	0.0
SF	−0.1	0.0	−0.4	0.1	+0.2	+	−0.1	+
SSA	−0.1	+0.1	−0.4	0.1	+0.2	+	+0.1	+
SA	−0.4	−0.1	−0.1	0.0	−0.3	0.1	+0.1	+

NOTE: The + sign means a very slight gain too small to be measured.

Alloys tested

Vitallium[5]
Stainless Steel AISI Type 316—Supplier A
Stainless Steel AISI Type 316—Supplier B
Stainless Steel AISI Type 302

Referring to Table I, the areas of the various plates were carefully measured. These varied to the extent of about 6 per cent. Results of corrosion tests are correct within ±6 per cent.

Two sets of plates were strained by bending these to a 90° angle and then straightened. This treatment caused the Vitallium plates to display large crystals at the site of the bend and also caused cracks to form.

In another test, we had in mind that there might be a *galvanic effect* between screw and plate. Accordingly, screws of the same composition and manufacturer as the plates were firmly lashed to the plates with cat gut sutures and then submitted to the same 6 weeks' tests as those covered by Tables I to III inclusive.

Comparing the values of Table IV with those of Tables I to III inclusive, it is evident that if any galvanic action is present it is very slight.

DISCUSSION OF RESULTS

No gross changes in weight were observed when the four different kinds of bone fixation plates were exposed to body fluids. Over-all examination

[4] Bacteria which cause boils, etc.
[5] Registered trade mark of the Austenal Laboratories for an alloy containing 65% Co, 30% Cr, and 5% Mo.

shows that the Type 302 stainless steel made the best performance, but the margin is very slight.

As to the effect of straining on the corrosion loss of the plates there was a perceptable increase in loss.

Sharp ridges, edges, corners, and ends should be avoided in design of bone fixation plates to eliminate high local stresses. Screw holes should have

TABLE II. *Screws as received from manufacturers*

Duration of tests—6 weeks; loss in mg./dm.²/day; body temperatures

Corrodant	Vitallium	Type 316-A	Type 316-B	Type 302
PS	−0.0	−0.1	−0.1	−0.1
S	−0.1	−0.0	+0.1	+0.2
SF	0.0	−0.1	0.0	+0.0
SSA	−0.1	−0.1	+0.1	+0.0
SA	−0.1	−0.2	−0.1	−0.1

TABLE III. *Strained plates*

Weight changes (mg./dm.₂/day) of six weeks' tests of two sets of plates (a and b) same as in Table I except that they were strained. Test of 6 weeks at body temperature

Corrodant	Vitallium		Type 316-A		Type 316-B		Type 302	
(Run)	a	b	a	b	a	b	a	b
PS	0.0	0.0	−0.4	−0.1	−0.2	−0.1	−0.2	0.1
S	−0.4	−0.1	−0.5	−0.2	−0.1	−0.2	−0.0	0.0
SF	+0.2	+	−0.4	−0.2	−0.3	−0.2	+0.1	+
SSA	−0.2	−0.1	−0.3	−0.1	−0.1	−0.1	+0.1	+
SA	−0.1	−0.1	+0.0	+	−0.1	−0.1	+0.1	+

TABLE IV. *Galvanic effects, if any, between screws and plates*

Six weeks' test; body temperature; results in mg./dm.²/day

Corrodant	Vitallium	Type 316-A	Type 316-B	Type 302
PS	−0.1	−0.1	−0.1	−0.1
S	−0.1	−0.0	+	+
SF	0.0	−0.1	0.0	+
SSA	−0.1	−0.1	+	+
SA	−0.1	−0.2	−0.1	−0.1

rounded entrance and exit perimeters. Bending of plates during application should be avoided.

As to the corrodants used in the tests, none proved to be more active than the others. Our tests provided slight motion of the plate relative to the corrodant to simulate in vivo conditions.

TESTS IN VIVO

Besides the corrosion tests described above, tests in vivo were carried out by Dr. Clay Ray Murray, Professor of Surgery, in his laboratory at the

School of Physicians and Surgeons, Columbia University, New York City. The tests were carried out on dogs when repairing broken leg bones. The plates used were identical in composition with those described in the first part of this paper but they were smaller in size.

Upon examination of the implanted plates after 4 to 6 months we observed that there was complete absence of discoloration of the bone tissue in contact with the plates and that, furthermore, the plates in no way interfered with the healing process. There was no physiological tissue disturbance. Dr. Murray had considered the in vivo tests very conclusive.

The use of stainless steel, such as Type 302, has been recommended to both the Army and Navy (1943).

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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MAGNESIUM DRY CELLS[1]

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ABSTRACT

Magnesium dry cells patterned after the conventional Leclanché type "D" size flashlight unit have shown considerable promise in the initial stages of development. The discharge characteristics were in general similar to those of zinc cells. The best cells have contained a magnesium-aluminum-zinc alloy anode, MnO_2 and acetylene black cathode, and an alkali or alkaline earth bromide electrolyte, inhibited with ammonium chromate and gelled with a flour-starch mixture. On the basis of incomplete storage tests at room temperature, the authors believe that eventually successful shelf performance may be achieved.

[1] Manuscript received April 1, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948; investigation performed under sponsorship of U. S. Army Signal Corps.

INTRODUCTION

Magnesium batteries are of interest for two reasons: first, the inexhaustible supply of sea water from which magnesium is extracted, and second, the possibility of producing a better cell with magnesium anodes than is now available. Were theoretical values to be realized, one pound of magnesium would deliver 2.7 times as many ampere-hours of current at three times the anode voltage as would one pound of zinc.

There are various types of cells in which magnesium might be used. The reserve, or deferred action type, requires a high voltage and usually no shelf life. Magnesium cells of this type were used in various applications during the war (1). Wet cells, such as the railway signal battery, are a second type. Magnesium wet cells with chromic acid electrolyte have been described by Barbian and McNulty (2). A third type, dry cells, is the subject of the present investigation. This work is directed toward commercial as well as military uses, and has as its aim the provision of fundamental data for use by battery manufacturers.

TABLE I. *Magnesium alloy compositions*

Alloy		Nominal composition—%			
ASTM	Dow	Al	Mn	Zn	Mg
—	Pure Mg	—	—	—	99.95
—	Cell Mg	—	—	—	99.8
M1	M	—	1.5	—	Remainder
Z1	Z1	—	—	1.0	Remainder
AZ31X*	FS-1	3.0	0.3	1.0	Remainder
AZ61X*	J-1	6.5	0.2	1.0	Remainder
AZ80X*	O-1	8.5	0.2	0.5	Remainder

* Alloys have impurities (Fe, Ni, Cu, etc.) controlled to low levels.

CELL DEVELOPMENT

Anode

Cans were made first by drawing, later by impact extrusion, using pure magnesium, commercial wrought alloys, and commercial (cell) magnesium, whose compositions are given in Table I. The drawn cans (AZ31X) were standard "D" size (3) in outside diameter (1.245 in.), while the impact extruded cans (all other alloys) were somewhat smaller. The wall thickness for both types was 0.032 in. compared with 0.016 in. for zinc cans. The theoretical ratio of wall thickness for magnesium to that for zinc is 1.5, but this was increased to 2.0 to compensate partly for the lower current efficiency obtained with magnesium. The cans weighed about 9 grams, which is about half that of a zinc can of the same outside diameter. All cans were given a Bright-Pickle treatment.[2]

[2] Bright-Pickle Treatment:
Immerse part for two minutes in bath at room temperature:

CrO_3	180.0 g./liter solution
$Mg(NO_3)_2 \cdot 6H_2O$	30.0 g./liter solution
CaF_2	5.6 g./liter solution
H_2O	to make 1.0 liter

Rinse in cold running water.

Cathode

The Leclanché type of cathode, consisting of manganese dioxide and acetylene black, was chosen for this investigation. Preliminary wet cell tests indicated that the optimum ratio would be approximately 9 parts of Gold Coast manganese dioxide to one part of 50 per cent compressed Shawinigan acetylene black. The cathode mixtures were wet to the desired consistency with non-gelled electrolyte solution of the same concentration as that in the paste. A typical formulation was 450 g. MnO_2 + 50 g. acetylene black + 160 ml. solution containing 1000 g. $SrBr_2 \cdot 6H_2O$ per liter.

The bobbin diameter was at first 1.002 in. and later 1.026 in., though use of the smaller size was continued in the smaller impact extruded cans. These were all considerably smaller than the bobbins in most commercial zinc "D" cells which are usually about 1.05 in. and range from 1.00 in. (in jacketed cans) to 1.09 in. Bobbin length was $1\frac{21}{32}$ in., the same as in zinc cells.

Electrolyte

It is generally accepted that ammonium chloride solution cannot be used with magnesium because of the high rate of corrosion during storage. Consequently, a series of qualitative screening tests was undertaken to determine the most promising electrolyte materials, with the results pointing to the bromides of strontium, lithium, barium, and ammonium offering the greatest freedom from wasteful corrosion and anode polarization. These salts were selected for dry cell studies with the addition, in some instances, of ammonium chromate as an inhibitor.

The solutions were gelled with a mixture of three parts corn starch to one part winter wheat flour, using 6 ml. of solution to one gram of cereal mix. Gelling temperature varied with the electrolyte composition. Strontium bromide in 300 g./liter concentration was gelled $1\frac{1}{2}$ minutes at 95°C., while in 1000 g./liter concentration gelling occurred in one minute at 50°C.

TESTING PROCEDURE

Tests included two discharge tests—the JAN-BA-30 and the JAN-BA-8, and one shelf test. The former two are joint Army-Navy tests.[3]

JAN-BA-30—This is a flashlight test. Discharge was through $6\frac{2}{3}$ ohms resistance, four minutes per one-half hour, ten hours per day, five days per week, to an end voltage of 0.935. The specified 70°F. capacity after three months' storage is 14.0 days and after twelve months it is 12.0 days.

JAN-BA-8—This is a continuous discharge through the relatively high resistance of $83\frac{1}{3}$ ohms to an end voltage of 1.13. The specified 70°F. capacity after three months' storage is 220 hours and after twelve months it is 195 hours.

Shelf Test—An arbitrary test for evaluating shelf deterioration consisted of storage of the cells at 70°F., with momentary readings of closed circuit voltage through 5 ohms resistance being taken bi-weekly. Delayed action, if present, was also recorded. This is a form of anode polarization which prevents the immediate maximum flow of current. It is expressed in the number of seconds required for the potential to come up to 1.0 volt after the circuit is closed.

[3] JAN-B-18A, 7 October 1947, Joint Army-Navy Specification, Batteries, Dry.

PERFORMANCE CHARACTERISTICS

Initial

Fig. 1 shows a BA-30 discharge curve for a typical magnesium cell compared with that of a general purpose commercial zinc cell. The magnesium cell showed an excellent capacity of 18.1 days compared with 15.1 days for the somewhat older zinc cell.

Although the discharge curves for the two cells were very similar through the central portions, there was a major difference at the beginning of discharge amounting to about 0.5 volt in favor of the magnesium cell but decreasing to about 0.1 volt during the first day's discharge.

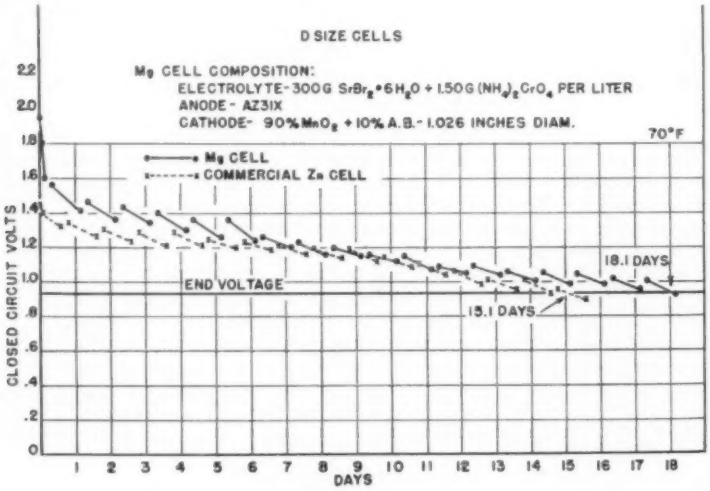

FIG. 1. BA-30 discharge curves

Fig. 2 shows typical BA-8 discharge curves for a magnesium cell and a commercial zinc cell. Here, again, the former disclosed a superior capacity; and the steep initial voltage drop was again evident.

The effect of discharge temperature on BA-8 capacity is portrayed in Fig. 3. This curve indicates that magnesium cells have desirable low temperature properties, since 62 per cent of the 70°F. capacity was recorded at 0°F. and 32 per cent at minus 20°F.

The electrochemical efficiency of the magnesium anodes has not been determined in dry cells, but wet cells studies have shown efficiencies of 60 to 65 per cent.

In order to determine what part of the magnesium cell was responsible for the steep initial voltage drop, four cells were discharged through 25 periods in the BA-30 test, including an overnight rest after the nineteenth discharge (Fig. 4). The cells were then rebuilt, each component being replaced separately with new material. When only the electrolyte, or anode and electrolyte, were renewed, voltage recovery was normal; but

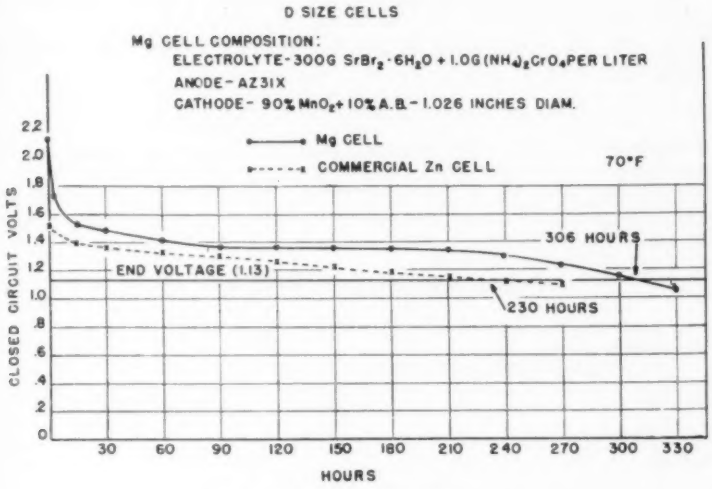

FIG. 2. BA-8 discharge curves

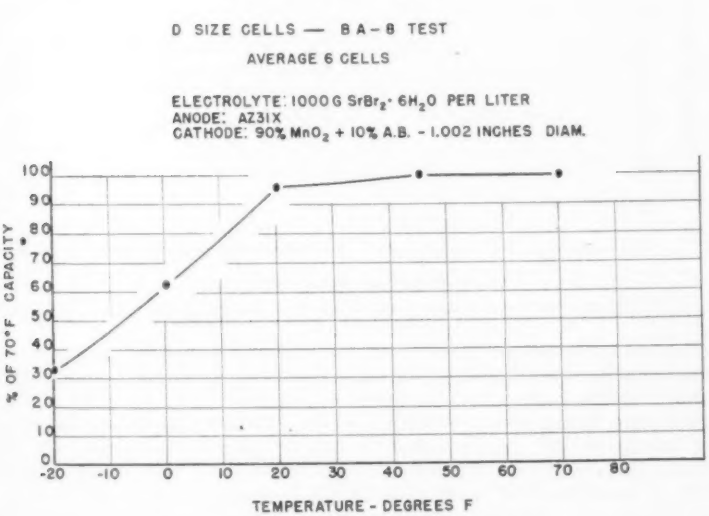
D SIZE CELLS — BA-8 TEST
AVERAGE 6 CELLS
ELECTROLYTE: 1000 G $SrBr_2 \cdot 6H_2O$ PER LITER
ANODE: AZ31X
CATHODE: 90% MnO_2 + 10% A.B. - 1.002 INCHES DIAM.
% OF 70°F CAPACITY
TEMPERATURE - DEGREES F

FIG. 3. Effect of temperature on capacity

when the cathode and electrolyte were replaced, the voltage rose to that of a new cell and the initial discharge curve paralleled that of the new cell. The cathode was, therefore, entirely responsible for the rapid voltage drop.

It appears likely that the voltage drop is in this case a result of the increase in pH which occurs at the cathode during discharge. This theory is compatible with the conclusions of those who have studied the Leclanché cell (4, 5).

Storage

A complete evaluation of storage properties is not yet possible, since none of the more promising cells have been in storage as long as the 12 months required of the BA-30 and BA-8 tests. Many cells have been stored eight months or more without perforation, and in one group of seven cells none have perforated in this length of time (Table III).

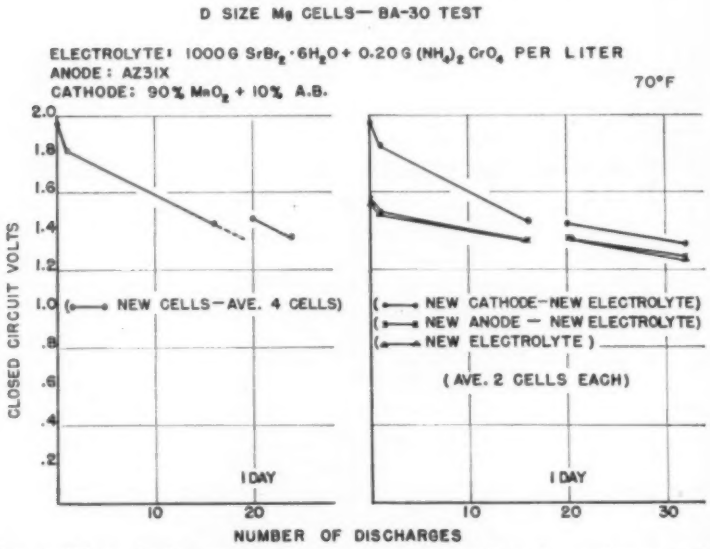

FIG. 4. Effect of cell component replacement on initial discharge characteristics

Furthermore, cell properties have not seriously decreased during storage. Some cells have been shelved for eight months with as good a closed circuit voltage as zinc cells after a similar storage period (Fig. 5). The zinc cells in this case were not commercial, but were made fresh at the beginning of the storage period. An initial difference of 0.4 volt in favor of the magnesium cells disappeared during the eight months' storage. Delayed action reached a maximum of three seconds, but later disappeared entirely. It is notable that the electrolyte in these magnesium cells contained no inhibitor, indicating possibilities for shelf life improvement through proper use of inhibitors.

Capacity after storage has in general been at least as good as initial capacity. The effect of storage on the discharge characteristics is shown in Fig. 6. After three months' storage, these cells actually had a greater

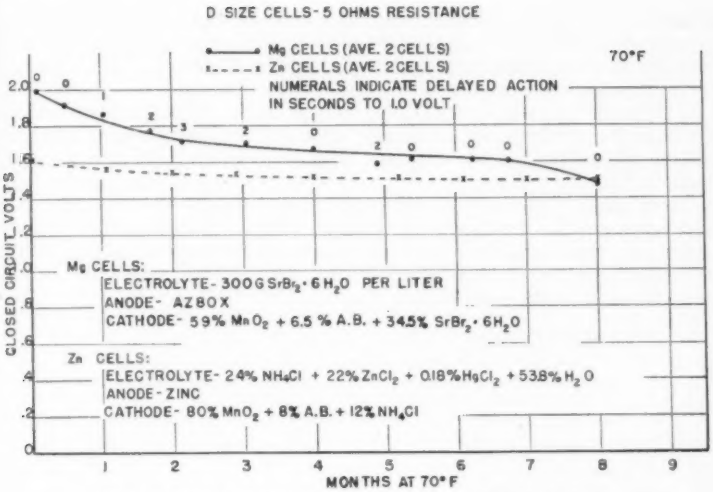
D SIZE CELLS-5 OHMS RESISTANCE
Mg CELLS (AVE. 2 CELLS)
Zn CELLS (AVE. 2 CELLS)
70°F
NUMERALS INDICATE DELAYED ACTION IN SECONDS TO 1.0 VOLT
CLOSED CIRCUIT VOLTS
Mg CELLS:
ELECTROLYTE- 300 G $SrBr_2 \cdot 6H_2O$ PER LITER
ANODE- AZ 80 X
CATHODE- 59% MnO_2 + 6.5 % A.B. + 34.5% $SrBr_2 \cdot 6H_2O$
Zn CELLS:
ELECTROLYTE- 24% NH_4Cl + 22% $ZnCl_2$ + 0.18% $HgCl_2$ + 53.8% H_2O
ANODE- ZINC
CATHODE- 80% MnO_2 + 8% A.B. + 12% NH_4Cl
MONTHS AT 70°F

FIG. 5. Effect of storage on voltage and delayed action

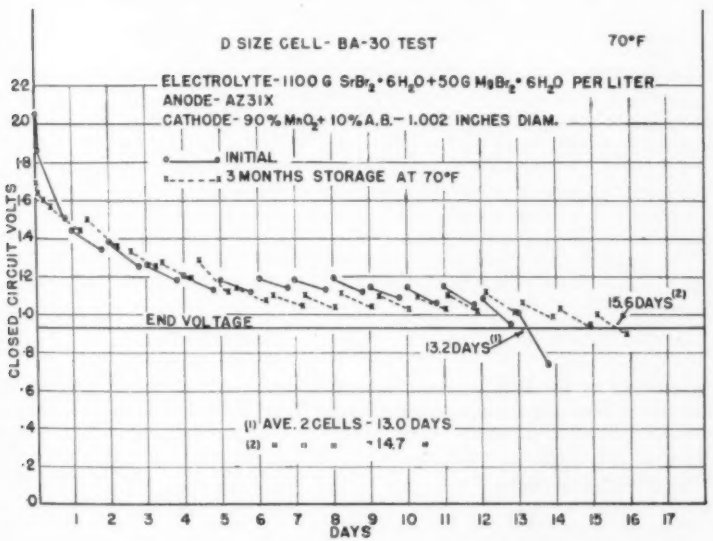
D SIZE CELL- BA-30 TEST
70°F
ELECTROLYTE- 1100 G $SrBr_2 \cdot 6H_2O$ + 50 G $MgBr_2 \cdot 6H_2O$ PER LITER
ANODE- AZ 31 X
CATHODE- 90% MnO_2 + 10% A.B. - 1.002 INCHES DIAM.
INITIAL
3 MONTHS STORAGE AT 70°F
CLOSED CIRCUIT VOLTS
END VOLTAGE
15.6 DAYS (2)
13.2 DAYS (1)
(1) AVE. 2 CELLS - 13.0 DAYS
(2) " " " - 14.7 "
DAYS

FIG. 6. Effect of storage on discharge characteristics

capacity than cells from the same batch had initially. It is noteworthy that the capacity after three months' storage was greater than the required fourteen days, even though these cells, because of smaller bobbins and a

different formulation, initially were not as good as those shown in Fig. 1. It is also significant that, as a result of the voltage drop during storage, the steep initial drop in discharge was eliminated, putting all of the energy output within the conventional operating voltage range.

In order to find what part of the voltage drop on shelf occurred at each electrode, a cell which had been stored for three months was dismembered and rebuilt, using the old cathode with new anode and new electrolyte (Table II). The voltage had dropped 0.33 volt during the storage period. The new anode and electrolyte increased the voltage by 0.21 volt, so this must represent the drop in anode voltage. Since the old cathode was still present, the remaining 0.12 volt must represent the drop in cathode voltage. Although the initial voltage drop in discharge is entirely cathodic, both electrodes undergo voltage drops in storage.

TABLE II. *Voltage drop in storage at cathode and at anode*

Electrolyte: 200 g. $SrBr_2 \cdot 6H_2O$ + 100 g. $MgBr_2 \cdot 6H_2O$ + 2.6 g. $(NH_4)_2CrO_4$/l.
Anode: AZ31X
Cathode: 90% MnO_2 + 10% acetylene black
70°F.—5 ohms resistance

Initial closed circuit voltage	1.92
Three months closed circuit voltage	1.59
New anode and electrolyte with old cathode—closed circuit voltage	1.80
Voltage drop at anode: 1.80 — 1.59 = 0.21	
Voltage drop at cathode: 1.92 — 1.80 = 0.12	

The decrease in anode voltage during storage is undoubtedly a result of film formation caused by reaction between anode and electrolyte. At the cathode, the voltage decrease is of less magnitude and could be caused by an increase in pH resulting from a slow attack on the anode. This theory was supported by another experiment in which cathode bobbins moistened with electrolyte containing strontium bromide and ammonium chromate were stored for three months before they were assembled into complete cells. The closed circuit voltage of the cells made from the stored bobbins was the same as for those made initially from the same batch of bobbins. That is, there was no drop in cathode voltage during storage when no anode was present.

ELECTROLYTES

The effect of electrolyte composition on cell characteristics is shown in Table III. The anode in these cells was AZ31X + 0.20 per cent Ca and the cathode was 90 per cent MnO_2 + 10 per cent acetylene black. A comparison of the various concentrated bromides tested (Part A) shows that the strontium salt was somewhat superior to the lithium and barium compounds in initial capacity but somewhat inferior in open circuit attack. Addition of 50 g. $MgBr_2 \cdot 6H_2O$ to 1100 g. $SrBr_2 \cdot 6H_2O$ per liter greatly improved both capacity and corrosion resistance, though the average time of 6.3 months to perforation could still not be considered satisfactory for most purposes. All of these electrolytes gave a relatively smooth discharge corrosion, lithium bromide being somewhat inferior to the others in this respect.

The importance of ammonium chromate as an inhibitor is indicated in Part B (Table III). Addition of 1.5 grams of the chromate to 300 grams of strontium bromide per liter not only increased the shelf life (to perforation) from 1.7 months to 4.5 months, but also increased the average BA-30 capacity from 14.7 to 18.0 days.

The effect of electrolyte concentration on cell properties is also shown in Part B (Table III), where cells containing 300 grams of $SrBr_2 \cdot 6H_2O$

TABLE III. *Effect of electrolyte composition on cell characteristics*

Anode: AZ31X + 0.20% Ca Cathode: 90% MnO_2 + 10% A. B. 70°F.

Electrolyte	$(NH_4)_2CrO_4$	Cathode diameter	Initial BA-30			3 months BA-30		Ave. months to perforation
			c.c.v.*	Days to 0.935 V.	Corrosion pattern	c.c.v.*	Days to 0.935 V.	
A. *Various concentrated bromides*								
	g./liter	*inches*						
1000 g. $SrBr_2 \cdot 6H_2O$/l.	0	1.002	2.05 (0)	11.0	Smooth	1.60	9.3	2.8
1100 g. $SrBr_2 \cdot 6H_2O$ + 50 g. $MgBr_2 \cdot 6H_2O$/l.	0	1.002	2.05 (0)	14.1	Smooth	1.56	14.7	6.3
800 g. $BaBr_2 \cdot 2H_2O$/l.	0	1.002	2.04 (0)	9.1	Smooth	—	9.7	3.2
1000 g. LiBr/l.	0	1.002	1.98 (0)	7.8	Med. smooth	—	—	4.0
B. *Effect of $(NH_4)_2CrO_4$ and of $SrBr_2$ concentration*								
300 g. $SrBr_2 \cdot 6H_2O$/l.	0	1.026	1.96 (0)	14.7	Mod. perforation	—	—	1.7
300 g. $SrBr_2 \cdot 6H_2O$/l.	1.5[x]	1.026	1.97 (0)	18.0	Mod. perforation	1.63 (2)	—	4.5
1000 g. $SrBr_2 \cdot 6H_2O$/l.	0.20[x]	1.026	2.06 (0)	15.3	Smooth	1.73	—	3.2
C. *Various ammonium electrolytes*								
150 g. NH_4Br/l.	10.0	1.002	1.89 (0)	12.8	Bad perf.	1.64 (2)	12.0	>8.0**
150 g. NH_4Br/l.	50.0	1.026	1.90 (0)	18.0	" "	—	—	>5.0[xx]
200 g. NH_4Br + 110 g. NH_4OH/l.	15.0	1.002	1.60 (4)	11.2	" "	1.44 (10)	13.4	1.5
100 g. NH_4Cl/l.	50.0	1.026	1.91 (0)	10.9	" "	—	—	0.5

* Figures in ( ) represent delayed action in seconds to 1.0 volt.

[x] Saturated.

** None of seven cells perforated in eight months.

[xx] Two cells perforated in four months—four cells not perforated in six months.

per liter, saturated with ammonium chromate, are compared with cells containing 1000 grams of $SrBr_2 \cdot 6H_2O$ per liter, also saturated with the chromate. The more dilute electrolyte was superior in initial capacity and in months to perforation, while the concentrated system gave a smoother discharge corrosion (see also Fig. 7). The solubility of chromate in both of these bromide concentrations was too low to give good corrosion resistance.

Data for various ammonium electrolytes are shown in Part C (Table III). Ammonium bromide with chromate inhibitor was outstanding,

particularly in storage properties. The batch of seven cells with no perforations in eight months is the best recorded to date. Capacities were also good, though the cans perforated badly during discharge. The discharge curve for this electrolyte (Fig. 8) was unusual in that the voltage had a tendency to increase somewhat during discharge and to drop during rest periods. Ammoniacal ammonium bromide and ammonium chloride, both with added chromate, attacked the anode badly on open circuit and appear to have no interest.

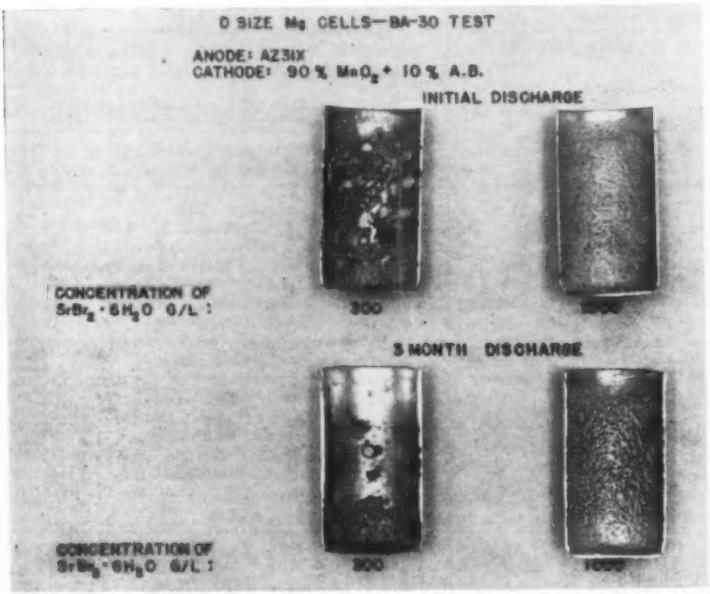
D SIZE Mg CELLS—BA-30 TEST
ANODE: AZ31X
CATHODE: 90 % MnO_2 + 10 % A.B.
INITIAL DISCHARGE
CONCENTRATION OF $SrBr_2 \cdot 6H_2O$ G/L :
300
3 MONTH DISCHARGE
CONCENTRATION OF $SrBr_2 \cdot 6H_2O$ G/L :
300

FIG. 7. Effect of strontium bromide concentration on closed circuit corrosion

The data of Table III indicate several promising leads for further work. Ammonium chromate should be added to bromides in which the chromate solubility is not as limited as in the strontium solution.

ANODES

The effect of anode composition on cell properties is shown in Table IV. The electrolyte in these cells was 1000 g. $SrBr_2 \cdot 6H_2O$ + 0.05 g. $(NH_4)_2CrO_4$ per liter and the cathode was 90 per cent MnO_2 + 10 per cent acetylene black. AZ31X was easily the outstanding anode, showing superiority in BA-8 and BA-30 capacities, BA-30 corrosion pattern (see also Fig. 9), capacity after storage, and in open circuit attack. The addition of 0.20 per cent calcium to AZ31X gave a marked decrease in BA-8 capacity and cut the time to perforation by 50 per cent.

Pure magnesium was superior to commercial magnesium in BA-8 and BA-30 capacity and in BA-30 corrosion pattern, but the open circuit attack

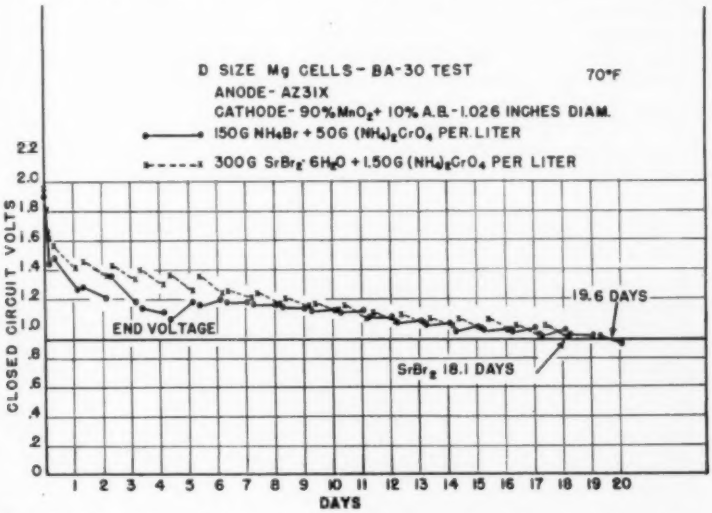

FIG. 8. Effect of ammonium bromide plus ammonium chromate electrolyte on discharge characteristics.

TABLE IV. *Effect of anode composition on cell characteristics*

Electrolyte: 1000 g. $SrBr_2 \cdot 6H_2O$ + 0.05 g. $(NH_4)_2CrO_4$ per liter
Cathode: 90% MnO_2 + 10% acetylene black (1.002 in. diameter) 70°F.

Anode	Initial BA-8			Initial BA-30			3 Months BA-30		Ave. months to perforation
	c.c.v.	Hr. to 1.13 V	Corrosion[x] pattern	c.c.v.[*]	Days to 0.935 V.	Corrosion[x] pattern	c.c.v.[*]	Days to 0.935 V.	
Pure Mg	2.19	168	Bad. perf.	2.13 (0)	10.5	Smooth	—	—	1.2
Commercial Mg	2.18	142	Smooth	2.12 (0)	9.6	Slight perf.	—	—	1.1
M1	2.19	142	Smooth	2.13 (0)	10.2	Uneven	1.20 (50)	7.5	2.75
Z1	2.13	152	Bad. perf.	2.12 (0)	9.0	Slight perf.	1.60 (1)	1.0	4.6
AZ31X	2.06	172	Slight perf.	2.05 (0)	12.8	Smooth	1.83 (1)	13.4	7.0
AZ31X + .20% Ca	2.06	145	Slight perf.	2.06 (0)	12.7	Smooth	1.75 (2)	12.7	3.4
AZ61X	2.05	148	Mod. perf.	2.06 (0)	11.8	Slight perf.	1.68 (0)	9.6	2.0
AZ80X	2.01	139	Bad. perf.	1.98 (0)	10.4	Mod. perf.	1.69 (0)	10.6	3.1

[*] Figures in ( ) represent delayed action in seconds to 1.0 volt.
[x] See also Fig. 9.

was bad in both cases. M1 was also attacked badly in open circuit, developing a heavy gray coating adjacent the anode, which resulted in a serious delayed action and low voltage. In the BA-8 test, commercial

magnesium and M1 were the only compositions which did not perforate (Fig. 9). Addition of 1 per cent zinc to commercial magnesium (Z1) increased the shelf life from 1.1 to 4.6 months, but the capacity after three months' storage was extremely low in spite of a good voltage.

Increasing the aluminum content from 3 per cent to 6.5 per cent to 8.5 per cent (AZ31X → AZ61X → AZ80X) progressively lowered capacity and increased the tendency toward pitting and rough corrosion in both discharge tests (Fig. 9). The Z1 cannot be compared with the other zinc-containing alloys in these tests, since the Z1 was not controlled purity as were the others. Storage properties also decreased with increasing aluminum except that AZ80X was somewhat better than AZ61X.

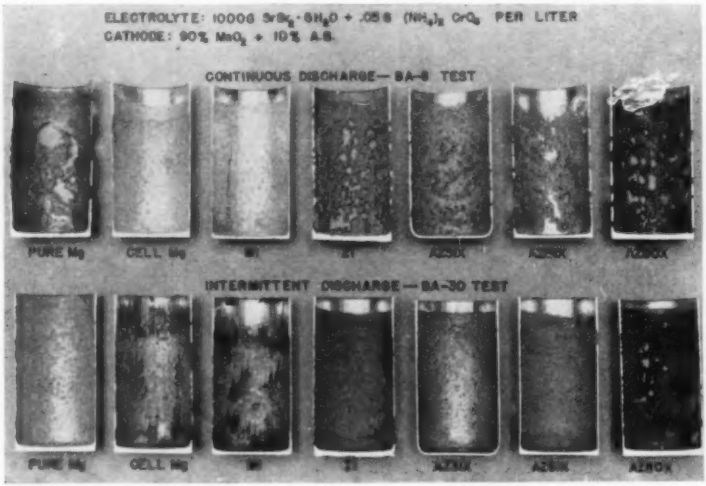

FIG. 9. Effect of anode composition on closed circuit corrosion

SUMMARY

In the development of a magnesium dry cell, the Leclanché type flashlight cell was used as a pattern. Magnesium dry cells had initial 70°F. capacities comparable to commercial cells and capacities at 0°F. which were unusually high. Magnesium cells were stored eight months with as good a closed circuit voltage as zinc cells after a similar period. In one batch of seven cells, none had perforated in eight months' storage. Capacity after 3 months' storage at 70°F. was in general at least as good as initially, and BA-30 capacities in excess of the required fourteen days were obtained after three months' storage. Although magnesium cells had an initial voltage about 0.5 volt greater than zinc cells, most of this difference disappeared during storage or in the initial stages of discharge. In storage, the voltage loss was partly anodic and partly cathodic, while in discharge the drop was entirely cathodic.

All of the alkali and alkaline earth (including ammonium) bromides tested as electrolytes appeared promising. Ammonium chromate not only was an effective corrosion inhibitor but it also increased capacity. An electrolyte concentration of 300 g. $SrBr_2 \cdot 6H_2O$ per liter was superior to one containing 1000 g. per liter of the same electrolyte when both were saturated with chromate. Of the commercial wrought alloys tested as anode material, AZ31X was outstanding in both discharge and storage properties.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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SINTERED PLATES FOR NICKEL-CADMIUM BATTERIES[1]

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ABSTRACT

Porous plaques are prepared by sintering carbonyl nickel powder of low apparent density. The plaques are impregnated with nickel or cadmium salt solutions and the heavy metal ions precipitated in the pores of the plaque by cathodic polarization in alkali hydroxide solution. Sintered plates made by this procedure have been assembled into experimental cells for study. A typical set of discharge curves is shown for a five plate experimental cell covering the range from the twenty hour rate to the three minute rate.

INTRODUCTION

One of the new developments of the past decade in the field of nickel-cadmium storage batteries has been the utilization of sintered metal plaques[2] of high porosity as the support for the active masses of the positive and negative plates. This feature marks a departure in the construction of plates for this type of alkaline battery, heretofore characterized by the assembly of perforated plates as described in the literature (1–4). The capsulation of the active masses in pocket-type plates represented the practical solution of the problems encountered in fashioning a suitable plate. The various nickel hydroxides or hydrates and the cadmium compounds are unsuitable for making pasted plates and development of fabricating procedures along this avenue of approach was rejected after exhaustive tests by the Swedish investigators (5).

[1] Manuscript received September 16, 1948. This paper prepared for the New York Meeting, October 13 to 16, 1948.

[2] Porous compacts or "plaques" refer to the sintered metal body having a plate-like shape; plate refers to the plaque after impregnation with active mass.

Sintered plaques of high porosity provided a new approach to the general problem of devising a support for the active masses in plates for nickel-cadmium batteries. Moreover, the need for additions of conducting substances such as graphite to the relatively poorly conducting active mass is eliminated. Apparently these features were recognized in the laboratories of the I. G. Farbenindustrie A.G. during their studies of the utilization of metal powders produced by the decomposition of metal carbonyls. The development was carried through to production by Accumulatoren-Fabrik A.G. During World War II, 10 and 20 ampere-hour batteries for aircraft and special types for military applications were manufactured up to the time that Allied bombing raids destroyed producing facilities. The German industry has been described in reports by American and British investigators (6–11).

Examination and study of the data which were made available in the reports on sintered plate batteries manufactured in Germany led to the conclusion that the new type of construction presented favorable possibilities along the lines of improved performance and decreased weight. These factors, in combination with the recognized favorable properties of alkaline nickel-cadmium batteries with regard to retention of charge, long life, absence of plate deterioration on standing in the charged or uncharged condition, and discharge at relatively high rates, led to a program of investigation. This research and development program on a laboratory scale of operations has been carried on under contract with the Battery Division of the U. S. Signal Corps.

PREPARATION OF PLAQUES

The manufacture of porous articles by the usual procedures used in powder metallurgy has been restricted to porosities in the range below 50 per cent (12). There is very little information available in the literature on the science and technology of articles with porosities varying in the range from 60 per cent to 90 per cent which is of interest for battery plates. In the preparation of plaques of high porosity, it is necessary to use powders of low apparent density and the working procedure has differed from the normal application of the methods of powder metallurgy by eliminating the step of compacting the powder under pressure.

The requirement for low apparent density is met by carbonyl nickel powder, prepared by the thermal decomposition of dilute nickel carbonyl vapor (13–15). This powder, which can be made with an apparent density as low as 0.6 gram per cc., sinters with ease in a protective atmosphere and without the need for compacting under pressure. The bonding of the loose carbonyl nickel powder to form a coherent mass occurs on heating at temperatures as low as 500°C. or on heating for a very brief period, as short as four minutes, at 800°C. In its relative ease of sintering, carbonyl nickel powder resembles carbonyl iron powder from which it differs in particle shape (16). Electron micrographs of carbonyl nickel powder show particles from 1 to 4 microns in diameter, of irregular shape and having numerous very sharply pointed peripheral projections. Photomicrographs show a marked tendency to form chain-like clusters up to 200 microns in length. Sedimentation studies indicate a peak distribution at particle diameters from 4 to 10 microns (17).

In our work, attention has been concentrated mainly on the sintering of plaques from a carbonyl nickel powder of an apparent density of about 1 gram per cc. This powder was prepared for use by screening a "B" grade of carbonyl nickel powder obtained from the International Nickel Company. This powder had an apparent density of 0.78 gram per cc. prior to removing the fraction coarser than 200 mesh.

Plaques of the desired porosity prepared by sintering unpressed powder in a form are fragile and fracture sharply without bending on applying a stress. Rectangular plaques are generally warped and dished, and are unsatisfactory for battery plates. This condition is overcome by the incorporation of a grid which not only permits the attainment of the desired resistance to fracture but practically confines shrinking in the direction of the thickness dimension. Several forms of grids have been studied. The German 10 and 20 ampere-hour batteries were provided with a grid having channel frames, 2.5 –4 mm. wide, surrounding a rectangular screen of 10 mesh cloth woven from 0.15 mm. wire. The grid and the wire were made of nickel-plated steel, annealed in a reducing atmosphere after plating (6). In our studies, we have used grids of perforated nickel sheet, rolled or electroformed metal 0.005 to 0.021 inch (0.127 to 0.53 mm.) as well as of wire cloth from 40 to 4 mesh. A rectangular strip of thin nickel sheet is welded to the cloth to serve as a lug. Plaques have also been prepared using iron wire and nickel-plated iron wire grids for studies of the effect of iron on the positive plate.

Our experience with the wire cloth grids has indicated that it is not desirable to use wire cloth which is finer than 20 mesh. With the finer grids, the holes become difficult to fill except by taking unusual and special precautions in assembling the compact. When the holes are properly filled, the sintering treatment locks the grid in place because of the bridging which connects the layers on the two sides of the grid. This bridging effect is important because a firm bond is not formed between the carbonyl nickel particles and the nickel metal of the grid. Experiments in which the surface of the grid was changed by various etching treatments, plating, alternate oxidation and reduction, and oxidation did not improve the cohesion. When the bridging is incomplete, as was found with the plaques prepared with the fine mesh grids, the positive plates prepared from these plaques tended to slough pieces of plate during charging.

Before use, the nickel grids were heat-treated in a dissociated ammonia atmosphere for ten minutes at 900°C. and then cooled in the same protective atmosphere. The grids were flattened in a hydraulic press, applying about 1500 psi (105 kg./sq. cm.). This precaution aids in eliminating ridges which tend to form at the periphery of the plaques.

The plaque is prepared in a graphite form made by machining a suitable cavity in a graphite plate, 1 inch (2.54 cm.) in thickness and provided with a flat graphite cover plate of the same thickness. The cover plate is held in place by suitably located pins. In making the compact, the desired amount of nickel powder is weighed out and about half of this powder is placed in the cavity of the form and spread with a brass scraper to form a smooth layer. The grid is then placed on the smooth layer and is covered by sifting in powder from a small hand container made of 40 mesh wire cloth. The filling of the cavity may be completed by continued sifting or by direct addition of the powder with a spatula. The powder is leveled with

a brass tool and excess powder is removed. The cover is then placed in position and the compact is ready for sintering. Transfer to the sintering furnace should be effected without jolting the form and its contents inasmuch as jarring has a tendency to cause the formation of hairline cracks in the compact. On sintering, these develop into noticeable cracks, sometimes of appreciable length and width. Except for their adverse appearance, it may be noted that cracks formed in this way have not led to plate failures.

Sintering of the compact is accomplished in an 8 kw. pilot plant sintering furnace (18) provided with a cooling chamber and with means for maintaining an atmosphere of dissociated ammonia or nitrogen. The furnace

TABLE I. *Preparation of typical plaques*

Plaque and form designation		SFM2			E	S
Powder description, see notes		(1)				(2)
Compact preparation						
Powder sintered	g.	20.97	28.67	41.65	11.45	42.15
Grid, wire cloth mesh, nickel		16 x 16	8 x 8	—	—	—
Wire diameter	mm.	0.30	0.59	—	—	0.71
Weight	g.	7.74	13.07	13.06	3.28	15.37
Depth of form cavity	mm.	2.21	3.00	4.37	4.78	6.35
App. density of powder filling	g./cc.	1.19	1.20	1.20	1.20	0.99
Experimental conditions						
Sintering time	min.	10	—	—	—	—
Initial furnace temperature	°C.	932	—	—	—	—
Final furnace temperature	°C.	911	921	920	932	920
Average furnace temperature	°C.	900	893	907	922	909
Results						
Plaque weight	g.	28.71	41.74	54.71	14.73	57.52
Plaque area	sq.cm.	80.76	81.01	81.21	20.58	67.59
Plaque thickness	mm.	1.90	2.56	3.69	3.85	5.39
Shrinkage in width	% of compact dimen.	1.24	0.99	0.92	0.78	1.39
Shrinkage in height	" " "	1.05	0.41	0.13	1.40	1.49
Shrinkage in thickness	" " "	14.0	14.5	15.5	19.4	14.9
Plaque volume	cc.	15.34	20.74	29.97	7.92	36.43
Pore volume	cc.	12.18	16.07	23.69	6.27	29.97
Porosity	% of app. sinter volume	83.0	83.5	82.9	83.1	85.9
Porosity	% of plaque volume	79.1	79.3	77.3	79.2	82.2

Notes: (1) Carbonyl nickel powder No. P23-2S, -200 mesh,
Apparent density by Scott Volumeter 0.97 g. per cc.
Analysis 0.14% C, 0.57% Fe, traces of Si and Cu.
(2) Carbonyl nickel powder No. P23-2, International
Nickel Co. "B" type, as received.
Apparent density 0.78 g. per cc.

temperature is measured and controlled by a pyrometer controller. The thermocouple is located in the gas space. The graphite form is then transferred into the furnace. The transfer is made immediately after the controller opens the heating circuit of the furnace. After the desired interval, which is commonly ten minutes for all of the plaque sizes which have been studied, the graphite form is pushed into the cooling chamber which is also provided with the protective atmosphere. On removal, the plaque is inspected, trimmed, especially to remove powder from the lug, weighed and measured. The plaques are now ready for the next operation; namely, the introduction of the active mass.

Experimental conditions and data for the preparation of typical plaques having three areas and thickness varying from 2 to 5 mm., representing average values from the many plaques (about 1000) which have been prepared, are summarized in Table I. The effect of the time of sintering is illustrated by the data in Table II. Porosities are calculated from the dimensions of the plaque and are expressed in percentages of the plaque volume and of the apparent sintered powder volume, that is after correcting the plaque volume for the volume occupied by the grid. The values of the porosity found in this way are in agreement within 1 per cent with values determined on impregnation of the plaques with water in a vacuum.

TABLE II. *Plaque preparation; effect of sintering time*

Sintering time ..... min.	10	15	20	30	60
Compact preparation					
Powder sintered, description	Same as Table I, (1)				
Weight ..... g.	23.74	24.48	23.99	24.66	24.48
Grid, nickel wire cloth	16 x 16 mesh, 0.30mm. wire dia.				
Weight ..... g.	8.46	8.71	8.84	8.84	8.54
Depth of form cavity ..... mm.	2.21	—	—	—	—
Apparent density of powder filling ..... g./cc.	1.21	1.25	1.23	1.26	1.25
Experimental conditions					
Initial furnace temperature ..... °C.	932	—	—	—	—
Final furnace temperature ..... °C.	907	929	932	—	—
Average furnace temperature ..... °C.	896	907	918	920	917
Results					
Plaque weight ..... g.	32.20	33.19	32.83	33.50	33.02
Plaque area ..... sq. cm.	90.82	90.88	91.07	90.82	90.30
Plaque thickness ..... mm.	1.90	1.83	1.73	1.65	1.58
Shrinkage in width % of compact dimens.	1.26	1.26	1.05	1.26	1.36
Shrinkage in height " " " "	1.13	1.02	1.02	1.13	1.53
Shrinkage in thickness " " " "	13.8	17.2	21.8	25.3	28.7
Plaque volume ..... cc.	17.26	16.63	15.76	14.99	14.27
Pore volume ..... cc.	13.63	12.90	12.08	11.22	10.56
Porosity ..... % of app. sinter volume	83.7	82.5	81.8	80.4	79.4
Porosity ..... % of plaque volume	79.1	77.7	76.5	75.0	74.0

IMPREGNATION

The introduction of the active mass into the pores of the plaques, which is generally referred to as the impregnation of the plaques, is accomplished by means of four steps carried out in sequence; namely the soaking of the plaques in solutions of nickel or cadmium salts, preferably the nitrates, cathodic polarization of the soaked plates in alkali solution, washing of the plates, and drying. This cycle of operations may be repeated to introduce the desired amount of active mass into the pores of the plaques. Much of our work has followed along the lines indicated by German practice (6, 8) in subjecting the plaques having a porosity between 75 per cent and 85 per cent to four cycles of impregnation for both the positive and negative plates. By this procedure, the active mass, assuming that the compounds precipitated in the pores are hydroxides, occupies between 30 to 40 per cent of the pore volume.

The first step of the impregnation procedure, which consists in filling the

pores with a solution of the desired metal is carried out by a vacuum procedure. The desired number of plaques to be treated is placed into a suitable vessel of nickel or glass and the system is evacuated to a pressure below 10 mm. Hg. Solution is then admitted in sufficient quantity to cover the plaques which are allowed to soak for five minutes, after which air is admitted to the system and the excess solution drained rapidly. Depending on the number and size of the plates, the solution volume has been varied from 200 ml. to 2000 ml. per plate. The volume of solution has not been found to have any effect on the gain in weight of the plates in the vacuum procedure. The plaques are transferred immediately to the electrolysis apparatus.

The nitrate solutions used for the soaking are approximately saturated at room temperature. The nickel nitrate solution for the positive plates contains 15.5 per cent nickel or 0.25 g. per ml. while the cadmium nitrate solution for the negative plates contains 26.5 per cent cadmium or 0.47 g. per ml. Each of the solutions is adjusted to contain a free acid content of 3 to 4 grams of nitric acid per liter. In both cases, the continuous evolution of gas during the soaking period indicates that there is a reaction between the sintered nickel plaque and the solution. In the case of a plaque which has been soaked for five minutes in nickel nitrate solution, observation of the soaked plate after immersing in water will show an outward diffusion of green nickelous nitrate and precipitation of nickelous hydroxide in about fifteen to thirty minutes. It is not possible to extract completely the nickel nitrate solution from the pores of the plate by washing with water. The cadmium nitrate solutions assume a green color due to the presence of nickelous ions.

The cathodic polarization of the soaked plates is carried out in a nickel can which acts as the anode. For the laboratory program it has been found convenient to electrolyze with one plate per can, a number of the cans being connected in series. The soaked plates are suspended in the middle of the cans, allowing about 1 cm. separation from the can walls. The circuit is closed on adding hot 25 per cent caustic soda or potash solution. The alkaline electrolyte is preheated to about 100°C. so that the temperature at the close of the electrolysis period will be between 70°C. and 80°C. The current is adjusted and maintained constant during the electrolysis to give a current density of 15.5 amperes per sq. dm. Polarization is generally accomplished in twenty minutes, an interval which is sufficient for the attainment of a constant potential drop across the electrodes. This potential shows a sharp rise in the first two minutes and then levels off to the final value.

The current density is sufficiently high to promote a vigorous evolution of gas. At the cathode, a portion of the nitrate ion is reduced to ammonia while a large portion diffuses out of the pores of the plate. The elimination of nitrate ion by reduction and diffusion, and, in the subsequent washing, appears to be quite complete. Analysis of plates impregnated four times showed a residual content of 0.045 per cent NO_3 for the positive plate and 0.27 per cent NO_3 for the negative plate, both based on the total gain in weight. Residual nitrate, due to improper conditions of polarization and washing, is reduced to ammonia during the formation cycles when the plates are assembled in batteries. The presence of nitrate ion in cells results in an accelerated rate of loss of charge when a battery is on open circuit.

The soluble nickel and cadmium salts are converted into insoluble precipitates within the pores of the plates. If a solution-soaked plate is immersed in 25 per cent caustic solution without closing the electrical circuit, loss of metal hydroxide will occur by exudation, a phenomenon reminiscent of the growths encountered in silicate gardens. In the case of the positive plates, it appears that the precipitated mass consists mainly of nickelous hydroxide. In the case of the negative plates, the bulk of the precipitate appears to be cadmium hydroxide but both metallic cadmium and cadmium oxide have been identified. The latter is found when conditions in the electrolysis apparatus permit localized spots of high current density, as by improper centering of the cathode plate.

After polarization, the plates are washed in running cold tap water for a minimum of three hours which is usually sufficient to reduce the pH of the effluent water to about 9.0. Increase in the number of cycles of impreg-

TABLE III. *Impregnation for positive plates*

In each cycle of impregnation, the plates were evacuated to a pressure of 1–2 mm. Hg, soaked for 5 minutes in a nickel nitrate solution, density 1.61 g. per ml., 48.5% $Ni(NO_3)_2$, 3 to 4 g. HNO_3 per l., cathodically polarized at 15.5 amps per sq. dm. in hot 25% KOH soln., washed, and dried at 80°C.

The plaques used in these tests are described under "S" in Table I.

Impregnation Cycle no.	Gain in weight	Cumulative gain in weight	Calculated theoretical capacity A. H. (1)	Gain in weight g. per cc. of plate volume	Gain in weight g. per cc. of pore volume (2)	Vol. of act. mass, % of pore volume
	g.	g.				
1	11.23	11.23	3.25	0.308	0.374	9.5
2	9.09	20.32	5.88	0.558	0.677	17.2
3	7.45	27.77	8.03	0.762	0.925	23.5
4	7.47	35.24	10.19	0.967	1.174	29.8
5	4.69	39.93	11.55	1.096	1.328	33.7
6	4.91	44.84	12.97	1.231	1.492	37.9
7	4.05	48.89	14.14	1.342	1.625	41.3
8	3.61	52.50	15.18	1.441	1.745	44.3
9	2.68	55.18	15.96	1.515	1.818	46.2
10	1.70	56.88	16.45	1.561	1.874	47.6

Notes: (1) Calculated from the gain in weight, assuming $Ni(OH)_2$ and the cell reaction,

$$2Ni(OH)_2 + Cd(OH)_2 = 2Ni(OH)_3 + Cd.$$

(2) Assume density of 3.94 g. per cc. (19).

nation slows the washing. With insufficient washing, the plates will form efflorescences of potassium carbonate during the drying. To test the washing, it is preferred to test the drip from the plates inasmuch as direct application of indicator solution to the plates gives false indications due to the tendency of both nickelous and cadmium hydroxides to show activated adsorption of indicators (20). After washing, the plates are dried at 80°C. Whether or not the drying conditions are critical for the ultimate performance of the plates has not been established.

The course of the impregnation of plaques for ten cycles of treatment to introduce positive active mass is shown in Table III. The results are expressed in terms of the gain in weight and derived figures based on the plaque dimensions. The results for the course of the impregnation of negative plates are similar, though the weight gains per cycle are higher and

the calculated theoretical capacities are correspondingly higher than the values for the positive plates. The impregnation of plaques is considered to be normal when after four cycles the gain in weight corresponds to about 1 gram per cc. of pore volume for the positive plates and about 1.75 grams per cc. of pore volume for the negative plates.

SINTERED PLATE CELLS

The evaluation of the performance of plates is not a simple task and involves the correlation of data obtained in time-consuming tests. Multifold purposes are at hand, of which the more important phases deal with the effects of the process for producing plates including the many ideas for improvements and variations in procedure, the determination of unit capacities for battery design, and the establishment of figures for life expectancy. Each of these avenues of approach to the study of plates involves the determination of capacity, either of the individual plates by means of auxiliary electrode studies or from discharge curves of cells made up of various combinations of positive and negative plates. In addition to these aims of the testing program, observation of the physical behavior of the plates assembled into cells and subjected to many cycles of charging and discharging is required in order to reveal the dimensional and volumetric stability of the plates.

A large number of the positive and negative plates have been assembled into test cells. The simplest cell consists of two sintered plates or a sintered plate in combination with twin pocket-type plates of opposite polarity and known capacity, or a single sintered plate in combination with nickel sheet dummy plates. Cells with up to 11 sintered plates have been tested. Life cycle tests of such cells continue to be an important part of the program and at this time a large number of cells have completed 300 cycles of charging and discharging. The extensive testing program which was intended to give an over-all picture with regard to process conditions and plate characteristics is now being changed over to an intensive study in which variables are being controlled within narrower and defined ranges. This is the main reason that no attempt is made at this time to give an interpretation of the results of experimentation.

However, some observations on the question of plate stability are of interest. The usefulness of the sintered plate battery will rest to a large extent on its ability to retain the active mass within the pores of the plates, as well as to resist disintegration or other adverse processes tending to cause shedding. These latter and undesirable actions will result generally in the short-circuiting of the plate groups when the elements for the test cells are assembled in the usual manner and with the usual plate separation. The short-circuiting effect due to the disintegration of the positive plate has been observed with plates which were provided with wire cloth grids of 30 or 40 mesh, with plates which had been impregnated eight to ten times, and with plates for which the sintering time had been less than 10 minutes at 925°C.

A second type of phenomenon leading to short-circuiting of plate groups is by blistering of the positive plate. This behavior was noted with plaques sintered for 14–15 minutes at 980° when such plates were part of a multiple plate group. Test cells containing single plates from the same

batch have undergone up to 200 cycles of charging and discharging without evidence of blistering. It would appear that more severe test conditions, such as high rate discharges must be chosen for detection of plate failures. To date, no example of the failure of a negative sintered plate for physical or other causes has been noted.

TABLE IV. *Assembly of 9A.H. cell*

Test cell No. 8931; Curves shown in Fig. 1

Plates		Positive	Negative
Type, designation		SFM-2A	SFM-2B
Sintering data, Table I		Column 1	Column 2
Number		2	3
Area per plate (one face)	sq. cm.	80.46	80.68
Thickness	mm.	2.63	1.89
Volume	cc.	21.16	15.43
Weight	g.	45.46	28.00
Pore volume	cc.	16.11	12.15
Porosity, % of plaque volume		76.1	79.7
After impregnation			
Weight gain	g.	17.48	21.82
Equivalent theoretical capacity	A. H.	5.05	8.00
Total theoretical cell capacity	A. H.	10.1	—
Final plate weight	g.	62.94	49.83

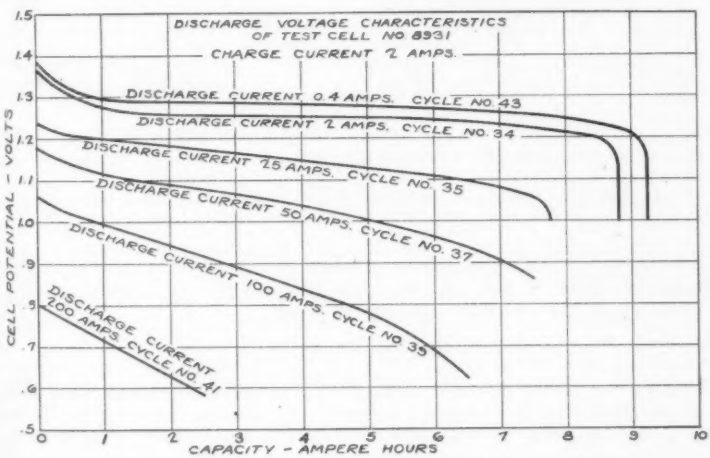

FIG. 1. Discharge curves for a sintered plate cell

Plaques sintered from light carbonyl nickel powder at 925° for ten minutes, having a porosity of about 80 per cent and impregnated in four cycles have been free of the physical defects mentioned above when tested individually or in groups up to 200–300 cycles of charging and discharging. The discharge curves of a typical sintered plate cell consisting of two

positive plates and three negative plates, characteristics of which are shown in Table IV, are shown in Fig. 1. The curves cover discharge cycles from the 34th to the 43rd. Between each cycle at a rate other than the two ampere discharge (approximately the 5 hour rate) there was a cycle of charge and discharge at the 2 ampere rate, which in general coincided with the 2 ampere curve shown for cycle No. 34. In accordance with the usual practice with alkaline nickel-cadmium batteries, the plates were formed after assembly so that no intermediate operations, such as drying of the plates, are involved. The plate separation was 0.79 mm. and the plate separators consisted of plastic rods spaced at 2.5 cm. intervals.

Attention is directed to the relatively high coefficients of utilization of the positive active mass for the curves shown in Fig. 1. Even at a discharge rate of 50 amperes for this small cell, corresponding to a current density of 1 ampere per sq. in. (15.5 amp./sq. dm.), the capacity to an end voltage of 1

FIG. 2

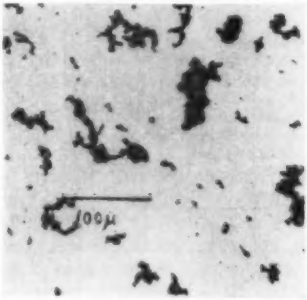

FIG. 3

FIG. 2. Electron micrograph of carbonyl nickel particle 8000. (Courtesy of the Battery Branch, Microoptical Section, Squier Signal Laboratory.)

FIG. 3. Photomicrograph of carbonyl nickel powder, No. P23-2 120. (Courtesy of the Battery Branch, Microoptical Section, Squier Signal Laboratory.)

volt corresponds to a 50 per cent coefficient of utilization. As shown by the subsequent cycles of testing, there has been no change in the capacity of the battery at the five hour rate of discharge.

CONCLUDING REMARKS

This survey of the laboratory study of sintered nickel plates for nickel-cadmium batteries has been of necessity of rather wide scope. Experience in the behavior of sintered plates and in the various phases of their manufacture has to be accumulated so that the problems and their nature can be recognized and visualized in terms of production and application. The results indicate that sintered plates represent an approach to the design of alkaline nickel-cadmium batteries which will permit an extension in the use and application of this type of storage battery.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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A LOW TEMPERATURE LIQUID SULFUR DIOXIDE CELL[1]

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ABSTRACT

An investigation was made to determine the possibility of constructing a low temperature cell in a liquid sulfur dioxide medium. Vapor pressures and solubilities of several highly soluble salts in liquid sulfur dioxide were determined in an effort to obtain an electrolyte which would remain liquid at atmospheric pressure and up to room temperature. Magnesium and sodium were chosen as anodes because of high potential and low cost. The cell Na; IBr_3, $FeCl_3$, SO_2; Fe was the most promising one developed. Discharge characteristics and shelf life were investigated. The open circuit voltage varied from 3.5 volts at room temperature to 2.7 volts at $-60°C$. Under high drain, the voltage varied from 2.6 to 1.2 over the same temperature range, and the short-circuited current from 70 to 16 ma./cm.[2]

INTRODUCTION

The characteristics of a couple which determine its practicability as a source of power are: (1) potential, on open circuit and under drain; (2) discharge characteristics, such as its efficiency, length of life under drain, and polarization properties; (3) shelf life, i.e., the time which a cell will remain potentially useful while not being used.

The development of a low temperature cell initially gave the choice of

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finding a new couple to operate in aqueous media or to use an entirely different medium which had properties more desirable than water. Among inorganic solvents which have ionization properties similar to water but much lower freezing and boiling points are liquid ammonia and liquid sulfur dioxide. Sulfur dioxide, which has a higher boiling point than liquid ammonia, was considered first.

It is known that anhydrous SO_2 has solvent properties similar to the H_2O system (1). The ionization of SO_2 as compared with water may be shown as follows:

$$\begin{aligned} 2\,SO_2 &\rightleftarrows SO_3^{=} + SO^{++} \\ 2\,H_2O &\rightleftarrows OH^- + H_3O^+ \end{aligned}$$

In liquid sulfur dioxide, $SOCl_2$ dissolves as an acid while NH_4SO_3 dissolves as a base and neutralization reactions occur just as in the water system. As an example,

$$Cs_2SO_3 + SOCl_2 \rightarrow 2\,CsCl + 2\,SO_2$$

Substitution reactions may be illustrated by their use in the preparation of thionyl derivatives. In this case, for example, $SOCl_2$ is mixed with substances containing the desired radical and which will form as products insoluble precipitates with a sulfur dioxide solution of the thionyl derivative.

Sulfur dioxide in the liquid form is not a reducing agent, as is shown by the fact that halogens and other oxidizing agents may be dissolved and recovered again in the original form. But oxidation-reduction reactions readily take place as when $FeCl_3$ or $SbCl_5$ is added to a solution of iodide ions in sulfur dioxide, in which case iodine immediately separates.

$$KI + FeCl_3 \rightarrow FeCl_2 + I + KCl$$

The discovery of a reaction of this type which would also give optimum cell characteristics was the subject of this investigation.

Solubilities vary widely in liquid sulfur dioxide. These may range from a few hundredths molar to over 50 weight per cent salt. Several substances such as $FeCl_3$ have reciprocal temperature coefficients of solubility which become important when the cell is being designed for low temperature use. Tables I and II show the solubilities of some common inorganic substances (2). As a rule, the compounds having an ionic crystal lattice are less soluble than those tending toward a covalent bonding (molecular lattice). This may be shown in the halide series where chlorides are only slightly soluble while the bromides and iodides have respectively higher solubilities. In certain cases, solubilities are increased by reason of complex formation with other salts. As an example, cadmium or mercuric iodide are more soluble in the presence of potassium iodide, probably due to the formation of a complex such as $KCdI_3$. Solubilities of inorganic salts and their effect on the vapor pressure of the liquid SO_2, which is approximately 3 atm. at room temperature, became important in the search for a practical cell.

Some highly soluble organic compounds seemed to offer the solution to this problem but were found to react with the anode materials or to reduce the conductivity of the electrolyte appreciably. On the whole, it appeared that the reduction of vapor pressure could not be achieved without affecting some of the other more desirable properties.

When considering possible components of the desired cell couple, the overall properties may be subdivided into those associated with the anodic and cathodic reactions and with the electrolyte. The anodic reaction is one of oxidation supplying electrons to the external circuit. The products of both reactions should be soluble in the electrolyte in order to prevent scale formation which leads to inactivity of the cell by polarization at the reacting surfaces.

It is desirable that the electrodes have the lowest possible resistance to current flow so that there is no undue dissipation of energy or potential

TABLE I. *Solubilities in liquid SO_2 at 50°C.*(2)

Solubility	Substances
Practically insoluble	AgI, As, As_2O_3, As_2S_3, $Ba(NO_3)_2$, BiI_3, $Bi(NO_3)_3$, FeS, HIO_3, H_2SeO_3, HgI_2, K, K_2SO_4, KNO_2, K_3AsO_3, K_2AsO_4, $K_2H_2PO_4$, K_2CO_3, $KHCO_3$, $K_4Fe(CN)_6$, $LiNO_3$, $MgBr_2$, Na, $NaNO_2$, Na_2AsO_4, P, Sb, Sb_2S_2, Sb_2S_3, Se, $TeCl_4$
Slightly sol., <0.01%	$CdBr_2$, $FeCl_3$*, KF, $KClO_3$, $KBrO_3$, $K_2Cr_2O_7$, $K_3Fe(CN)_6$, $K_2D_2O_4$, $MgSO_4$, NaCl
Appreciably soluble, 0.01–0.1%	$AgNO_3$, $Ba(CNS)_2$, CaF_2, KCl, KIO_3, KNO_3, NaF, NaBr, $NaBrO_3$, NH_4F, NH_4Br*, $SrBr_2$
Miscible at room temp.	$AsCl_3$, Br_2, BCl_3, CCl_4, CS_2, ICl, PCl_3, POCl, SO_2Cl_2

* Reciprocal temperature coefficient of solubility.

TABLE II. *Specific values of solubility for the more soluble inorganic substances in liquid sulfur dioxide* (2)

Substance	Solubility at 50°C.	Substance	Solubility at 50°C.
	g./100 g.		*g./100 g.*
I_2	0.6	PBr_3	19–20
ICl_3	0.5	PI_3	0.3
NaI_3	4.0 (25°C.)	RbBr	18.20
IBr	6	KI	38.3
KCNS	35	KBr	1.2
NH_4I	1	NH_4CN	30

drop. The anode is usually constructed of a metal which takes part in the reaction and consequently, due to the high conductivity of metals, offers relatively little resistance to current flow. If the reacting material is not in the form of an electrode, as is frequently the case where the cathodic reaction is concerned, there are several alternative procedures that may be tried. The cathodic agents may be dissolved in the electrolyte and allowed to react at an inert electrode or they may be coated on an inert electrode.

The electrolyte should have a high conductivity, and high solubility of cathodic reactants and of reaction products. In this case, these properties must be retained over the wide temperature range.

The anode, cathode, and electrolyte must exist in contact with each

other without appreciable reaction while the cell is not under drain. An internal reaction of this type determines the storage time of the cell when not in use. When the cell is under drain, the desirable reaction should take place rapidly, supplying energy to the external circuit at a fast constant rate. The latter property depends on the amount of polarization at the reacting surfaces, that is, it is dependent on slow steps in the actual reaction or on the rate of removal of the reaction products. Each individual system has its own characteristic polarization properties which can only be observed in operation.

Sodium and magnesium were chosen as anode materials because of their high position in the electromotive series and because of their relatively low cost. Solubility in the liquid SO_2 limited the choice for materials entering into the cathodic reaction. Iodine, bromine, and $FeCl_3$ are some of the oxidizing agents that were used. Many other salts and combinations of them were tested, their use being primarily to increase the conductivity of the electrolyte. An interesting fact may be noted in the use of iodine and bromine in the cells. Where each was used alone the cell was not too good, but where both were used together a very promising cell resulted. The mixture consisted of one mole of iodine for every three of bromine. It is not certain as to what the exact composition of the resulting dark brown liquid was but it will be referred to as IBr_3. It is known that iodine and bromine combine by direct action of the elements to form compounds such as IBr and IBr_3(3). Although the latterh as not been definitely isolated or shown to exist by means of spectrography, certain phenomena tend to indicate its existence. A mixture of I + 4Br in a liquid SO_2 solvent has a greater conductivity than I + 2Br and both have higher conductivities than the sum of the conductivities of each alone. Both iodine and bromine have a relatively high polarizability but, due to the difference in size of the atoms, an added polar effect is obtained. This results in a large increase of ionization in the electrolyte and, consequently, improves the conductivity.

EXPERIMENTAL PROCEDURE

The range of useful operation aimed at in this investigation was between 30° and −60°C. A standard test for couples involves the determination of open circuit voltage, flash current (maximum current on shorting), and voltage under drain through resistances which are 4 and 50 times the numerical value of the open circuit voltage. A complete set of data is obtained at four temperatures: 20°, 0°, −30° and −60°C. During these tests, the polarization characteristics are observed by noting how quickly the voltage and current drop under drain.

Vapor pressures of liquid SO_2 were determined with solutions containing several highly soluble salts and mixtures of them. For quick tests in cases where it was doubtful as to whether there would be any appreciable effect on the vapor pressure, the boiling point was determined at atmospheric pressure. The apparatus consisted of a closed vessel constructed of standard pipe fittings. As may be seen in Fig. 1, a $2\frac{1}{2}$ inch close nipple with caps formed the body of the container, with one of the caps outfitted with a thermometer well of $\frac{1}{4}$ inch pipe fittings, a manometer outlet, and an insulated anode clamp.

The experimental procedure was as follows: The container was cooled to

a temperature of −50°C. by immersion in a dry ice-acetone bath. Liquid SO_2 was then drawn from a cylinder into the cooled vessel, followed by the addition of desired salts. While the solution was maintained at a temperature below boiling, the container was capped, connected to the mercury manometer, and the pressure readings taken. Temperature was recorded with a pentane thermometer immersed in the well which was filled with acetone to insure better heat transfer. The capped container was then allowed to warm up very slowly in an insulated box, thus permitting equilibrium conditions to be reached. After determining the variation of the vapor pressure with temperature, the container was again cooled and

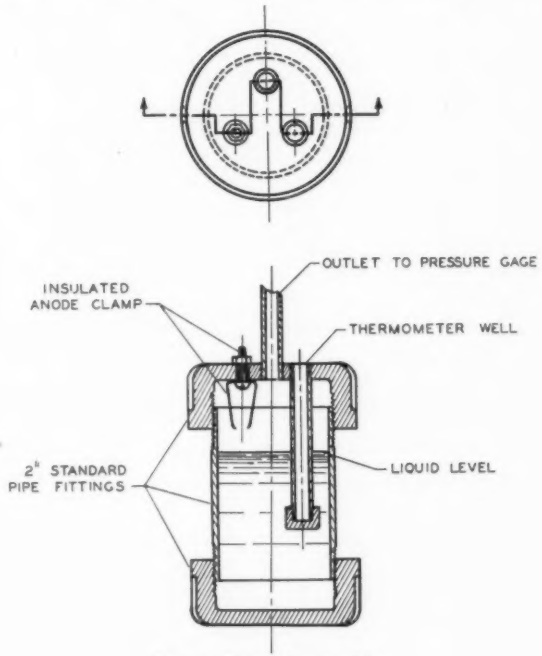

FIG. 1. The cell assembly

uncapped. At this point, preliminary examinations of certain couples were carried out with the remaining solution as an electrolyte.

About one mole of each salt was added to 100 cc. of liquid sulfur dioxide. Some of the typical data obtained may be seen in Fig. 2. As may be observed, highly soluble salts and elements do not affect the vapor pressure greatly. In the case of KI, the vapor pressure can be reduced but only with the sacrifice of total solubility at reduced temperatures. Table III compares solubility and boiling points of potassium iodide, ammonium thiocyanate, and formamide, three of the more highly soluble compounds. Other data not shown in Fig. 2 fall on the curve for pure liquid SO_2.

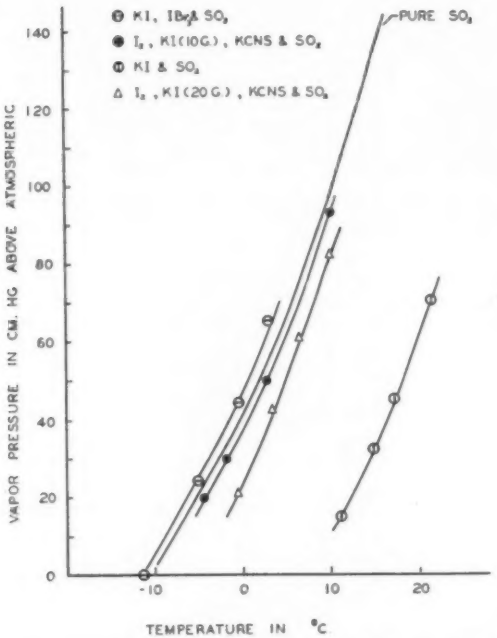

FIG. 2. Pressure-temperature relationship for liquid sulfur dioxide with and without dissolved salts.

TABLE III. *Freezing and boiling point comparison for liquid SO_2 mixtures*

Dissolved substance	Grams of material /100 cc. SO_2	Boiling point °C. of solution	Comments on freezing point
NH_4CNS	10	−7.6	Below −60°
	15	−7.9	Below −60°
	20	−8.0	Heavy red ppt. appears at −51°. Not solid at −60°.
	25	−5.4	Fine ppt. at −28°. Heavy ppt. at −51°.
$HCONH_2$	57	−1	No freezing to −70°
	113	4	No freezing to −70° but mixture becomes viscous.
KI	10	−7	Fine ppt. at −40°
	20		Heavy yellow ppt. at −35°
	28		First ppt. at −30°. Heavy slush at −50°.
	33		Ppt. at −29°
	50	−3	Ppt. at −23°, solid at −50°

The testing of cell couples consisted of the immersion of electrodes of constant exposed area in a liquid SO_2 electrolyte which contained various

salts and elements. The temperature was kept relatively constant, just below the boiling point of the mixture. The open circuit voltage was obtained with a 1000 ohm/volt voltmeter. The electrodes were then shorted through an ammeter to measure the flash current. This condition was maintained for from one-half minute to thirty minutes to note the polarization properties of each couple. The results are shown in Tables IV and V. Those in Table V were no longer considered for further study because of their poor characteristics while the better ones in Table IV were investigated further.

TABLE IV. *Promising cells in liquid SO_2*

No.	Cell composition per 100 cc. SO_2	O.C. Voltage	Flash current through 0.1 ohm ma./cm.²
41	Mg; 80g. I_2 + 10g. KI + 10g. KCNS; Fe	1.0	3.3
42	Mg; 40g. I_2 + 10g. KI + 20g. KCNS; Fe	1.0	5.0
43	Mg; Above + 10 drops H_2SO_4; Fe	—	6.5
44	Mg; 20cc. Br_2 + 10g. KI; Fe	0.95	17
53	Mg; 20g. NH_4CNS + 2g. I_2 + 5g. $FeCl_3$; Fe	0.75	8
54	Na; Sat'd KCNS + KI; I_2 subl. on carbon	2.9	12
55	Na; Sat'd KCNS + KI + I_2; I_2 subl. on C	2.1	0.4
59	Mg; 20g. $FeCl_3$ + 3g KI + 4g. NH_4CNS; Fe	0.95	6.7
63	Mg; 28cc. IBr_3 + 2g. KI; Fe	1.3	21
64	Na; 4g. KI + 10cc. IBr_3; Fe	3.1	21
65	Na; 80cc. SO_2 + 7cc. IBr_3 + 5g. $FeCl_3$; Fe	3.5	60
66	Na; Above + 5g. NH_4CNS; Fe	2.6	14

TABLE V. *Magnesium-SO_2 cells which failed to give satisfactory voltage or discharge*

No.	Electrolyte substance in SO_2	O.C. voltage	No.	Electrolyte substance in SO_2	O.C. voltage
30	KCNS + Br_2	1.3	47	KBr	0.7
32	$NaHSO_3$	0.0	48	KBr + I_2	1.3
33	$K_2S_2O_8$	0.0	49	KBr + KI + I_2	1.3
34	$KMnO_4$	0.0	51	KNO_3	1.1
38	Na_2SO_3	0.5	52	KNO_3 + KCNS	1.0
39	I_2 alone	0.5	54	$AlCl_3$ + KI	1.1
40	I_2 + KI	0.6	55	$AlCl_3$	0.7
45	H_2SO_4 (conc.)	0.3	56	$AlCl_3$ + KI + I_2	1.1
46	SO_3	0.9	57	$FeCl_3$	0.9

During the early investigations, cells were tested with magnesium anodes. This was done because of the ease of handling this type of cell. The better cells obtained with the magnesium anode were then tested with sodium as an anode. The resulting couples proved to be so superior, as far as open circuit voltage and flash current were concerned, that the majority of the remaining work was done on them. In one case, the cathode was not of an inert material. Cell number 54 had a cathode made up of iodine sublimed on a carbon rod. Results were promising, but with the use of the iodine-bromine mixture better cells were obtained. The complete low temperature tests were done on the better cells to show performance at all

temperatures. These data will be found in Tables VI and VII. Very good results were obtained with relatively little polarization effect under drain.

Results up to this point may be considered as only of a preliminary nature because of the importance of those to come. A cell may be very good where potential is concerned, but when shelf life and characteristics under drain are taken into account it may fail to be practical. With regard to these aspects, certain disadvantages of the cells were uncovered.

Shelf life was determined for magnesium and sodium in two different electrolyte mixtures at several temperatures. The procedure was to weigh samples before and after immersion in the electrolyte. The weight of sodium after immersion was obtained indirectly by titration because of the difficulty of washing the samples for balance weighing. The sodium was

TABLE VI. *Standard temperature test of sodium cell*

Anode: Na, area = 10 cm.² Cathode: Fe; area = 82 cm.² Electrolyte: 100cc. SO_2 + 10cc. IBr_3 + 5g KI

Temp.	O. C. voltage	High resistance 50 times O.C. voltage	Low resistance 4 times O.C. voltage	Flash current
°C.				*ma.*
15	3.0+	2.92	2.59	700
−21	3.0+	2.91	1.85	420
−38	3.0	2.71	1.61	200
−60	2.75	2.40	1.25	160

TABLE VII. *Standard temperature test of magnesium cell*

Anode: Mg; area = 7 cm.² Cathode: Fe; area = 82 cm.² Electrolyte: 100cc. SO_2 + 10cc. IBr_3 + 2g KI

Temp.	O.C. voltage	High resistance 50 times O.C. voltage	Low resistance 4 times O.C. voltage	Flash current
°C.				*ma.*
21	1.10	1.00	0.45	130
−31	1.00	0.81	0.30	70
−43	0.98	0.72	0.20	33
−60	0.92	0.50	0.15	20

dissolved in ethyl alcohol, acidified with standard acid, and back-titrated with sodium hydroxide, phenolphthalein being used as the indicator.

Constant low temperatures were maintained with dry ice-acetone, $CaCl_2$-ice-water, and ice-water baths. The beaker containing the electrolyte and the metal samples was immersed in one of the aforementioned bath mixtures which was held in a Dewar flask. To prevent heat transfer to this constant temperature system, it was put in a cryostat. The investigation of discharge characteristics was carried out in the vessel shown in Fig. 1, which was fitted with an insulated iron clamp to hold the anode material.

DISCUSSION

The results of the shelf life tests will be found in Table VIII. It was found that water in the electrolyte increased the weight loss for both sodium

and magnesium. With anhydrous electrolytes, however, both materials have fairly good shelf lives, magnesium being the better. It was observed that sodium may be kept in liquid sulfur dioxide for many days with no noticeable attack. This observation has recently received support from the work of Gilbert (4).

In Fig. 3 may be seen the results of the better cells under continuous discharge and various conditions. A commercial Leclanché type cell was given a similar test for comparison. The cell with the KI, IBr_3, SO_2 elec-

TABLE VIII. *Shelf life of sodium and magnesium in various cell electrolytes*

Metal	Anhydrous solution (electrolyte)	Temp.	Approx. time of test	Weight loss
		°C.	*hr.*	*mg./cm.² day*
Mg	100 cc. SO_2 + 10 cc. IBr_3 + 5 g. KI	−78	24	0.90
		−60	24	0.46
		−16	17	9.6
	100 cc. SO_2 + 10 g. $FeCl_3$ + 5 g. I_2 + 5 g. NH_4CNS	−78	24	0.87
Na	100 cc. SO_2 + 10 cc. IBr_3 + 5 g. KI	−60	17	18
		−16	17	72

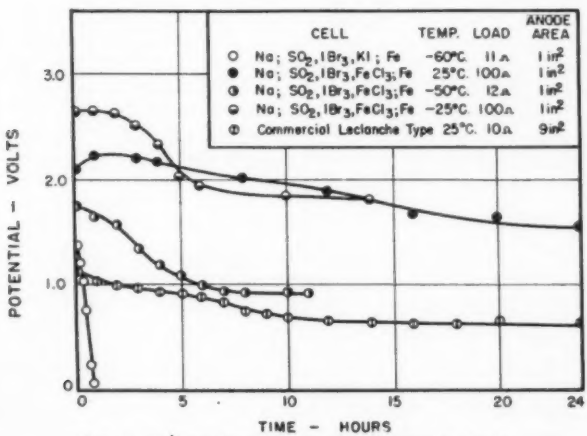

FIG. 3. Comparison of several cells under drain

trolyte polarized quickly, becoming practically inoperative within an hour's time. On the other hand, the cells containing $FeCl_3$ in place of the KI made very good showings under all conditions and compare favorably with the commercial cell even though having less exposed area. As the cell discharged through a known load resistance its potential was recorded on an automatic potentiometer. By use of Ohm's law, the current could then be calculated.

The operation of the liquid sulfur dioxide cells compared favorably with

the commercial cells as far as discharge characteristics are concerned, but the reproducibility could be improved. The somewhat erratic behavior may be attributed to an internal shorting of the anode material with the clamp. Cells constructed without insulating material on the clamp, or with defective insulation, would give good initial characteristics, but the cell assembly would heat up noticeably with correspondingly diminishing values for the open circuit voltage and the flash current.

The discharge experiments uncovered the problem of the necessity for complete insulation for the anode clamp. Of the several materials used a coating of Na_2SiO_3, baked on at 100°C., was found to be the best although still not satisfactory. A cell so constructed retained an open circuit voltage of 3.1 volts for three days, while the flash current gradually decreased. Upon inspection after opening it was found that the coating was cracked in many places and could easily be scraped off.

CONCLUSIONS

The most promising cell of those studied in this investigation consisted of sodium as an anode with iron as an inert electrode. The electrolyte was liquid sulfur dioxide with IBr_3 and $FeCl_3$ dissolved in it. The open circuit voltage varied from 3.5 volts at room temperature to 2.7 at −60°C. Under high drain, the voltage varied from 2.6 to 1.2 over the same temperature range, and the short-circuit current from 70 to 16 ma./cm.^{2}

Shelf life experiments showed magnesium cells to be better than sodium, although it was observed that sodium may be kept in dry liquid sulfur dioxide for many days with almost no noticeable attack. With inhibitors or other methods to lower local action of the anodes in the actual cells, sodium may prove to be better than is indicated in this report. Investigation of discharge characteristics revealed that this cell can compare favorably with a commercial Lechanché type dry cell, and if some of the remaining problems can be solved satisfactorily, a unit for special application can be predicted.

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Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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ELECTRODEPOSITION AND ELECTROCHEMISTRY OF THE DEPOSITION OF SYNTHETIC RESINS[1]

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ABSTRACT

A number of synthetic resin latices have been developed in recent years for mechanical coating and sizing processes. The object of the present work was to investigate the electrodeposition of synthetic resins from these latices. Anodic deposits several millimeters thick were built up rapidly, at unusually low potentials, and very high current and energy yields. Deposition was effected on soluble anodes or on diaphragms interposed between anode and latex. The influence of electrode material, current density, latex concentration, and duration of deposition on the yields, water content and properties of electrodeposits is discussed and compared to the case of rubber deposition. Experimental results indicate that the anodic generation of cations appears to be the controlling step in the deposition. Applications are suggested.

INTRODUCTION

It was about 25 years ago that the electrophoretic deposition of rubber was first investigated, resulting in the development of a successful industry based on the electrodeposition of rubber articles, chiefly from latex (44). But, very little has been done to extend the method and applications to the field of synthetic polymers. Investigations have been few and fragmentary.

The patent literature shows that the pioneers of the anode rubber electrodeposition process also took out patents on deposition from specially prepared cellulosic ester dispersions (43). We also find a few patents on the electrophoretic deposition of shellac, lacquers, and waxes (6, 7, 49). The technical literature is even less helpful in the field of aqueous dispersions of polymers: in effect, all it reports, without giving details, is that the electrophoretic deposition of synthetic resins can be accomplished (39, 55). Information on the electrodeposition of plastics from organic dispersions is also relatively scarce: the deposition of polystyrene, acrylics, and a mixed alkyd and ureaformaldehyde resin (17, 18), melamine resins (36, 54), and especially vinyl resins (14, 22) has been studied.

The theoretical aspects of the problem, namely the mechanism by which the electrodeposition of rubber latex particles actually takes place, has been discussed chiefly by Sheppard (42) and by Beal (3), and also by other au-

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thors (19, 51). None of these authors comes to any very definite conclusions, and there is a considerable range of interpretation of the phenomena taking place during deposition.

Quantitative studies of relations between some of the variables in rubber electrodeposition were made by Sheppard (42), Klein (25), Turner and Coler (50), and Twiss (51).

The advantages of deposition from non-aqueous suspensions were described by Gemant (17) and Feinleib (14). Briefly, these are: practically no side reactions at the electrodes, low current and energy consumption, good electrical properties of film, no need to emulsify plasticizers and other ingredients in order to incorporate them into the plating mix.

On the other hand, previous investigations have shown a number of disadvantages for organic suspensions: the film thickness that may be built up is of the order of only a few mils; the concentration of the suspensions is very low (below 5 per cent), necessitating frequent regeneration and considerable organic liquid handling. Dealing with organic solvents in an electrodeposition bath creates special problems, such as solvent losses and recovery, toxicity, and fire hazards. Finally, it was difficult to obtain a reproducible degree of precipitation of the resin, on account of the very narrow range of solvent to precipitant ratios over which precipitation takes place.

The early patents on cellulosic ester deposition from aqueous suspensions were of little value to industry for they, too, included considerable quantities of organic solvent and their concentration was low. Furthermore, good lacquers could be formulated from these cellulose derivatives with readily available and readily handled solvents. But, in the past few years, we have witnessed the development of synthetic resin latices, which incorporate no solvents at all, and whose concentrations run up to 60 per cent solids. These latices are generally made directly from the resin monomer by emulsion polymerization. Styrene, vinyl, and acrylic polymer latices are commercially available at the present time, and new latices are constantly being developed (33, 38). For some of these polymers available in latex form, there are no good solvents (especially not for polyvinyl and polyvinylidene chlorides). Even when satisfactory lacquer solvents are available, the use of a latex, when possible, cuts out the flammability and toxicity dangers, and the solvent recovery problems mentioned above, thus permitting the application of higher concentrations of polymer.

Synthetic resin latices have been commercially developed primarily for coating (by dipping, spraying, or brushing), sizing, and waterproofing purposes. The technical literature put out by the manufacturers of the latices never mentions the possibility of electrodeposition of their products (11, 16, 21, 47). It is well to emphasize that the mechanical applications of latices by dipping, spraying, and brushing have a number of limitations: the film thickness that can be built up in a reasonable period of time is limited; a fresh coating of latex will not readily wet a film of the resin that has already been partly dried; there is difficulty in wetting metals with latex uniformly; and even more difficulty in having the coat stay on uniformly (even then when the latex is thickened).

OBJECT OF THE PRESENT RESEARCH

1. To find out whether it is possible to electrodeposit synthetic resin films from commercially available latices, and under what conditions this can be achieved.
2. To study the various factors affecting the deposition and the side reactions taking place, and to compare these with the available information on rubber deposition.
3. To attempt to secure, from experimental data, more information on the actual mechanism by which anodic deposition of the resins takes place.

EXPERIMENTAL

Materials

For most of our experiments we used a Saran[2] latex. This is a copolymer of vinylidene chloride $CH_2{=}CCl_2$, and acrylonitrile $CH_2{=}CH{-}CN$, high in vinylidene chloride. The material, when shipped from the factory, contains 56 per cent solids and 20 per cent plasticizer based on resin content; the Saran material used in our studies, unless otherwise specified, contained about 50 per cent solids. The exact composition and, notably, the nature of the anion-active emulsifying agents used in Saran latex were not revealed by its manufacturer.

The latex has a recommended stability range of 0° to 55°C., and is most readily handled at room temperature. Upon standing, especially when in contact with air, some coagulation will take place, and, accordingly, before using the material, it was given a quick filtration through glass wool.

Saran latex is miscible with water in all proportions. It has a remarkable pH stability range: the literature (47) says that no coagulation will take place between pH values of 2 and 11; however, in our laboratory, the material was mixed with concentrated HCl (38 per cent), and no coagulation was observed for a considerable length of time. Normally, the pH is about 6.4. The tolerance for monovalent salts is also considerable. Polyvalent cations will cause considerable thickening and coagulation, for the latex particles carry a negative charge. Organic solvents vary in their action: ketones will cause immediate coagulation; esters have a slower coagulating effect; and ethyl alcohol shows hardly any action at all.

The particle size ranges from 0.08 to 0.15 μ. The viscosity is about 12 centipoises at 50 per cent concentration, and the material we used was not thickened in our experiments.

A number of materials, when properly emulsified, can be mixed with Saran latex; these include fillers, pigments, and plasticizers. Even some of the normally coagulating liquids (such as ketones), when properly emulsified, will form with the latex a mixture that is stable for a few days.

We also used Geon[3] (polyvinyl chloride $-CH_2CHCl(CH_2CHCl)_n-CH_2CHCl-$) latices, which are available on the market in unplasticized and plasticized forms (16, 21, 37). Again, the exact composition is not given by the manufacturer. The material shipped to us contained 56.3

[2] Saran F-122-A-20 latex, The Dow Chemical Company, Midland, Michigan.
[3] Geon Latex 11-X and Geon Plastic Latex PX-8, The B. F. Goodrich Chemical Company, Cleveland, Ohio.

per cent solids; we used it at a concentration of about 50 per cent. The stability toward heat is remarkable, as the latex will not coagulate at 100°C., being much superior to Saran in that respect. On the other hand, it is not so resistant to coagulation by acids as Saran latex, being unstable below a pH of 3. The normal pH of this material is 8.5. Monovalent salts behave much the same as in the case of Saran; polyvalent cations cause coagulation. The charge of the particles, as in the case of Saran, is negative. Tolerance for organic liquids is smaller than that of Saran. The particle size is about 0.2 μ. As with Saran, the material may be compounded with other emulsified substances.

For variation from polyvinyl halides, we performed a few experiments with a styrene-butadiene copolymer latex[4] (high in styrene), having the approximate formula, $-CH_2CH\varphi-CH_2-CH=CH-CH_2-CH_2CH\varphi-$. This material is shipped with a 45 per cent solids content, a particle size of 0.2 μ, and a negative charge on the colloid particles. The pH stability range is excellent, the material keeping indefinitely at a pH of 2, while its normal pH is 8 to 9.

Salt tolerance is about the same as in the case of Saran and of Geon latices (11).

We also did some work with polyvinyl acetate emulsions.[5, 6] These materials differ from the "negative latices" that is, latices containing negatively charged particles described so far, by having a charge slightly positive under normal conditions (pH about 4), but it may be reversed by making the suspension alkaline (under alkaline conditions, hydrolysis of the polyvinyl acetate will take place slowly). The solids content is about 55 per cent, with no plasticizer incorporated (9). The pH range for stability against coagulation is good, and so is the tolerance toward cations. Polyvalent anions will slowly cause coagulation. The viscosity is about 10 to 20 times that of the negative latices described above.

Mixture of the negative latices are stable in all proportions, and can be used for codeposition; mixtures of a polyvinyl acetate emulsion with Saran or with Geon, or with styrene-butadiene latex,will coagulate partially or completely, depending upon pH and concentrations.

Apparatus

As will be explained below, it is necessary to interpose a porous diaphragm between the latex and the electrode where no deposition of resin takes place (generally the cathode). In a great number of our simpler experiments, we used a rectangular porous cup, 6.3 x 2.1 x 8.6 cm., with a wall thickness of 4 mm.; this cup was immersed in an electrolyte (generally a solution of NaCl) which contained the cathodes. For our more quantitative tests, special cells were made. They are shown in Fig. 1. Cell I, Fig. 1, was used in cases where circulation of the latex was desired, and consists of a latex compartment (generally anodic) separated by two porous plate diaphragms from two interconnected compartments containing NaCl solution as an electrolyte (generally cathodic compartments). Latex is fed at the bottom and overflows at the top at a constant level. The dia-

[4] Dow Latex 512K, The Dow Chemical Company, Midland, Michigan.
[5] Darex Copolymer X56-L, Dewey and Almy Chemical Company.
[6] Gelva S-50 emulsion, Shawinigan Products Corporation.

phragms are 8 mm. thick, and the rest of the cell is made of acrylic plastic. Cell II, Fig. 1, was used for large size samples; it has a capacity of 400 ml. It does not provide for circulation. When used, it is filled with latex and immersed into a battery jar containing an electrolyte and, generally, the cathodes. The cell again was made of acrylic plastic.

In experiments where the polymers were deposited on a porous diaphragm surrounding the anode, the cathode was a circular copper cup, containing a solution of NaCl in which was immersed a large porous cup (cathode diaphragm) containing the latex: into this latex was introduced a smaller porous diaphragm, on which the deposition was to take place (anodic diaphragm). The inside of this anodic diaphragm contained either mer-

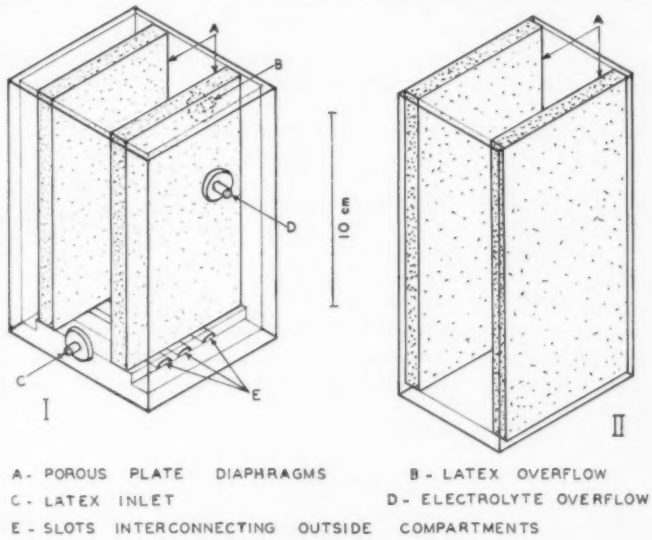


FIG. 1. Diaphragm cells

I—Cell providing for circulation of latex. Two interconnected electrolyte compartments surrounding latex compartment. Acrylic plastic construction.

II—Latex compartment made of acrylic plastic and porous plate. To complete the cell, it is immersed into a battery jar containing an electrolyte.

cury or an electrode immersed in a conducting or poorly conducting liquid. The anodic diaphragm was either fine, porous clay or alundum.

The rest of the apparatus was fairly simple. The electrode holder rack, with adjustable electrode spacing and height, was constructed in a manner which made it possible to run three experiments simultaneously, either in parallel or in series. The panel board was designed to give any d.c. voltage from 0 to 240 volts and currents up to 10 amperes, or to deliver power from any external supply, such as 110 volts a.c. (which could be reduced to any desired potential), or 750 volts d.c. from a rectifier set. A switching system provided for taking measurements on three parallel circuits with a single meter, without breaking the circuits at any time.

Procedure

Except for a few exploratory tests described below, all runs were made with direct current. The great majority of the experiments was carried out with a diaphragm separating the latex from the electrode where no deposition took place (generally the cathode). The cathode compartment, except when otherwise specified, contained a 4 per cent NaCl solution. The cathodic diaphragm was soaked in this solution for at least 30 minutes before use.

The majority of our runs was made without any circulation of latex. When circulation was used, it was very mild: about 6 ml./min., or 3 per cent of the cell contents per minute. The reasons for this will be explained below. All tests were made at room temperature.

Amalgamated zinc anodes, used in many of the experiments, were made by dipping zinc strip into an acid mercury nitrate bath for a few seconds, followed by washing first with concentrated ammonia, then with soap and water.

Other procedure details will be explained below.

EFFECTS OF AN APPLIED ELECTRIC FIELD ON A LATEX

Before discussing the experimental results, it will be of interest to describe what happens when direct current is passed through a suspension of rubber or a synthetic resin, with reference to a negative latex. Most of the facts presented in this section have been reported in connection with rubber electrodeposition (3, 25, 42).

I. Phenomena in the bulk of the suspension

In the bulk of the suspension, we have to consider the electrophoresis of the dispersed phase, electro-osmosis of the water phase, and electric migration of dissolved ions.

The Helmholtz equation for electrophoresis,

$$u = \frac{\epsilon \zeta E}{4\pi\eta}$$

where u = migration velocity of suspended particles, ζ = electrokinetic or "zeta" potential, E = potential gradient, η = viscosity, ϵ = dielectric constant of liquid phase, shows that the rate of electrophoresis (or electro-osmosis) is proportional to the applied voltage. If we keep the applied potential constant, but increase the conductivity of the suspension by adding an electrolyte, the total current and power consumption will increase, but the current carried by the colloid particles will not change. This means that, other factors being kept constant, the amount of rubber or resin transported per unit current or energy will be inversely proportional to the total conductivity of the suspension. But other factors *cannot* stay constant when the conductivity is changed: the addition of a salt such as NaCl will generally affect the electrokinetic potential of the particles in a way which cannot be predicted (42). From a practical standpoint, salts such as NaCl will lower the potential drop at the electrodes and through the diaphragms, which often constitute a major part of the total applied voltage: as a result, it may actually be advantageous, in certain cases, to *increase* the total conductivity.

As current is passed through a latex, even without any diaphragms, a

depression of the liquid surface is readily seen at the anode, and an attraction of liquid to the cathode shows visual evidence of electro-osmosis. If the cathodes are separated from the latex by a porous diaphragm and the cathode chamber is filled with a conducting solution, such as a solution of NaCl, upon application of a potential, the liquid level will drop in the anode compartment and rise on the cathode side of the diaphragm. Thus, one of the advantages of a cathodic diaphragm becomes apparent; it makes it possible to get rid of some liquid while depleting the latex of suspended solids by anodic deposition. In the case of rubber latex, Beal (3) claims that the electro-osmotic liquid removal keeps the latex concentration practically constant. In our experiments with synthetic resin latices, constancy of composition could not be mainted by electro-osmotic dehydration alone; but, even so, the use of a cathodic diaphragm helped to reduce the rate of depletion of suspensions by electrodeposition. It has been proposed to accelerate the removal of the liquid phase by superimposing a hydrostatic pressure onto the electro-osmotic pressure on the anode side (29) or by keeping the cathode under reduced pressure.

II. Cathodic phenomena

In the absence of reducible substances and cathodic migration of particles, the phenomena taking place at the cathode will be the evolution of hydrogen gas and the formation of hydroxyl ions. If no barrier is present between cathode and latex, the hydrogen causes trouble by forming a froth with the emulsion, the gas bubbles being transported to the anode partly mechanically, partly by electrophoresis (the electrophoresis of these gas bubbles is very readily observed). Once the gases reach the anode, they will blanket part of the electrode surface and mix with the depositing layer of polymer, causing increased resistance, unequal current distribution, and increased porosity of the deposits. Here the main need for a cathodic diaphragm becomes apparent: it keeps cathodic gases away from the latex and anodes, and makes it possible to work within a wide range of current densities and with close electrode spacings. It also keeps away the hydroxyl ions formed at the cathode (if the time of deposition is short enough): thus, the pH of the suspension can be maintained at a controllable value. In some experiments, the introduction of a cathodic diaphragm actually resulted in a decreased over-all resistance. The elimination of the gas blanket at the anode and of the foam in the latex more than compensated for the extra resistance of the diaphragm. Porous-clay cathodic diaphragms, with resistance never exceeding a few ohms, were used.

In cases where it would not be practical to use a cathodic diaphragm, or where the deposition is cathodic, hydrogen evolution has to be suppressed. To effect this, the literature (28) indicates the use of cathodes with a high hydrogen overvoltage in the presence of inorganic or organic reducible substances: an example is a lead cathode coated with a lead peroxide film. Such an electrode was used successfully in some of the vinyl acetate cathodic deposition runs: no hydrogen evolution took place. But in the great majority of our experiments, copper cathodes (low hydrogen overvoltage) were used in conjunction with a cathodic diaphragm.

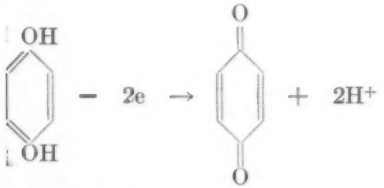
III. Anodic phenomena

One of the main purposes of our research was to try to determine what reactions actually take place at the anode. The various possible anodic

occurrences, reported in the literature on rubber deposition, are as follows:

1. Discharge of anions to form:
   a. OH^- ions, with oxygen evolution and H^+ ion formation.
   b. Ions forming gaseous products other than O_2 (e.g. Cl^-)
   c. Inorganic or organic ions, resulting in oxidation products:

$$\text{e.g., } SH^- - 2e \rightarrow S + H^+$$



2. Oxidation of electrode material
   a. To form soluble products: e.g., $Zn - 2e \rightarrow Zn^{++}$
   b. To form insoluble products: e.g, $Pb + 2\ OH^- - 4e \rightarrow PbO_2 + 2\ H^+$

(It is important to note that hydrogen ion is formed at the anode in a great number of these reactions.)

3. Discharge of negative colloid particles.
4. Migration of cations and water away from the anode.

RESULTS AND DISCUSSION

General

With all three negative latices used, namely, Saran (vinylidene chloride-acrylonitrile copolymer), Geon (polyvinyl chloride), and styrene-butadiene copolymer, good deposits of substantial thickness were obtained in a short time, with little or no modification of the latices. The deposition is characterized by high current yields, comparable with those obtainable with rubber latex, and exceptionally high energy yields, due to the fact that deposition voltages were about one tenth that in the case of rubber latex.

Table I shows the maximum current and energy yields obtained in our experiments, using zinc anodes, copper cathodes, and a cathodic diaphragm.

TABLE I

	Vinylidene chloride-acrylonitrile copolymer (Saran)	Polyvinyl chloride (Geon plastic latex)	Styrene-butadiene copolymer
Maximum current yield, in grams of dry polymer per faraday	2650	3440	2480
Maximum energy yield in kilograms of dry deposit per kw.-hr.	101	97	—

The tabulated figures all correspond to satisfactory anode deposits. The maximum energy yields were obtained with total cell voltages of the order of 1 volt (from anode to cathode, including diaphragm), current densities of the order of 4 milliamp./cm.^{2}, and deposit thicknesses of the

order of 1 mm. plated in about 20 minutes. At higher current densities, deposits over 3 mm. thick can be obtained quite rapidly.

Unmodified vinyl acetate emulsions did not yield any definitely visible *electro*deposits. With suitable modifications, deposition could be observed either at the cathode or at the anode, depending upon conditions. In no case, however, did these deposits exhibit satisfactory properties.

INFLUENCE OF CURRENT DENSITY

Qualitative

The current density will not only influence the rate of deposition, but, to a certain extent, will also affect the properties of the electrodeposit.

The lower limit of practical current densities and corresponding voltages is set by a non-uniform deposition. This lower limit varies somewhat with the type of electrode used and with the pH of the suspension. For zinc electrodes and unmodified Saran latex (pH = 6.4) the limiting current density is about 3.5 milliamp./cm.^{2}, below which the plastic will deposit mostly at the edges of the electrode and in little "islands" elsewhere on the surface. Slightly above this lower limit, deposits are coherent and in one piece, yet not uniform at the surface, having a wrinkled finish that resembles the surface of some leather goods (for which Saran electrodeposits would make good substitutes). As the current is increased, the deposit becomes smooth, yet its thickness still is not uniform, being greater at the edges. At still higher current densities (about 15 milliamp./cm.^{2} for Saran latex and zinc anodes), the deposit thickness is nearly uniform. In other words, the "throwing power" improves with increasing current densities. This is in agreement with results reported on other electrophoretic depositions (40).

With the spotty type of deposit is associated a spotty, pitting type of electrode corrosion, that is especially evident with nickel anodes. As the current density is increased, the pits become more frequent and less deep, and, finally, uniform electrode dissolution is reached. For zinc anodes, amalgamation promoted uniform dissolution.

It should be noted here that the *initial* current density is the determining factor. If the initial current strength is above the minimum for uniform plating, and, after a short period (of the order of 30 seconds), the current is decreased below this minimum for the rest of the plating cycle (say, 20 minutes), the resulting deposit will be uniform. If, on the other hand, deposition is started below the critical current density, and continued at a current density in the uniform range, the resulting deposit will have an irregular and wrinkled finish.

The upper limit of useful current densities is set either by the start of gas evolution at the anode (which means, passivation of the electrode), or by excessive resistance and heating in the deposited film. The gassing limit varies with the kind of electrode material used and, to a lesser extent, with the type and concentration of anion present in the latex. Thus, with nickel electrodes, the presence of alkali phosphate (i.e., phosphate and hydroxyl ions) in the latex will cause gas evolution at a current density (20 milliamp./cm.^{2}) at which regular anode solution takes place if only chloride ion is present. With lead electrodes, gassing starts at current strength values as low as 10 milliamp./cm.^{2}, and the non-uniform plating range

extends up to nearly 10 milliamp./cm.^{2}: therefore, the usefulness of lead anodes is very limited. Iron and mild steel anodes are not passive below 25 milliamp./cm.^{2}; at about the same current density, the resistance factor starts to become predominant.

At low and medium current densities, the rubber or resin is deposited at the anode in the form of a gel which is quite permeable to ionic migration and contains a considerable amount of liquid; as a result, there is very little voltage rise during a constant current deposition. However, a current density and voltage are reached, at which a combination of compacting, electro-osmotic dehydration, and local heating bring about a rapid increase in the resistance of the deposit, causing an increase in the potential drop across the deposit, and, therefore, in the rate of dehydration by electro-osmosis. This, plus local heating, causes further coagulation and tighter packing of the deposit, whose resistance increases still further; again the potential difference across the layer increases, and so on. Once this sequence of phenomena is started, it will proceed at an accelerated rate, until the deposit is practically impervious to any further passage of current. The combination of dehydration and heating may be such that partial carbonization of the deposit will take place while the electrode is still in the bath; at the same time, there will be hardly any heating at all in the main body of the latex. Within 2 or 3 minutes of high current density plating, the resistance of an electrodeposit may jump from a few ohms to several thousand ohms.

Quantitative

In Fig. 2 and 3, are plotted the variations in current yield, moisture content, initial and final cell voltage, and energy yield with current density. In each run, approximately the same number of coulombs were passed through the suspension resulting in deposits of approximately the same weight and thickness. Curves of Fig. 2 and 3 then show what happens when it is desired to get a certain deposit thickness under different conditions.

It is apparent (Fig. 2 and 3) that the current yield is substantially independent of the current density at which the resin is deposited. On the other hand, the degree of packing of the deposit will be influenced by the current strength. The moisture content of the electrodeposits decreases with increasing current density. This decrease is slow at medium current densities, but becomes faster above 20 milliamp./cm.^{2}, when the resistance of the deposits begins to build up fast, and the voltage across the deposit and, consequently, the rate of electro-osmotic dehydration increase accordingly. In connection with this packing and dehydration, we see that, at low current densities, the spread between initial and final cell voltage at a given current value (which is a measure of the deposit resistance) is very small. At higher current densities, this spread becomes considerable (Fig. 3). For a given deposit thickness to be attained, there is a practical upper limit for the current density. In the present work, this limit is between 20 and 25 milliamp./cm.^{2}, above which the physical properties of the deposit begin to suffer, mainly as a result of overheating. If the desired deposit thickness is low, higher current densities may be used, as it takes some time to build up the resistance of the plated layer.

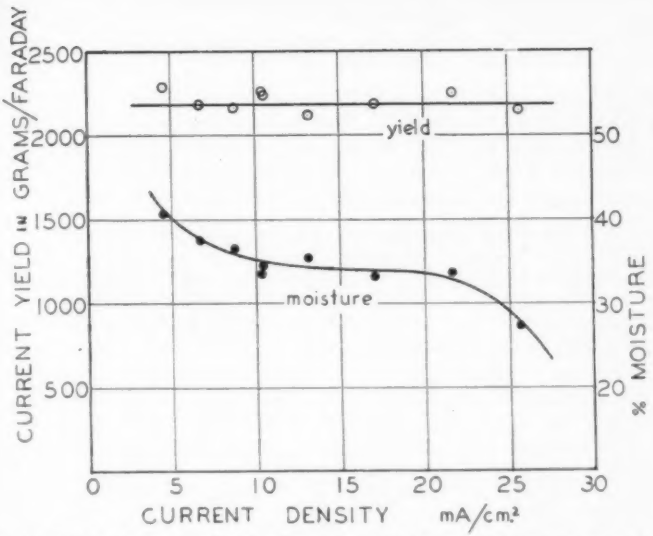


FIG. 2. Effect of current density on current yield and moisture content (per cent of dry weight of solids) of Saran electrodeposits. 50 per cent solids in Saran latex. Amalgamated zinc anodes. Approximately 0.011 faradays passed through suspensions in all cases.

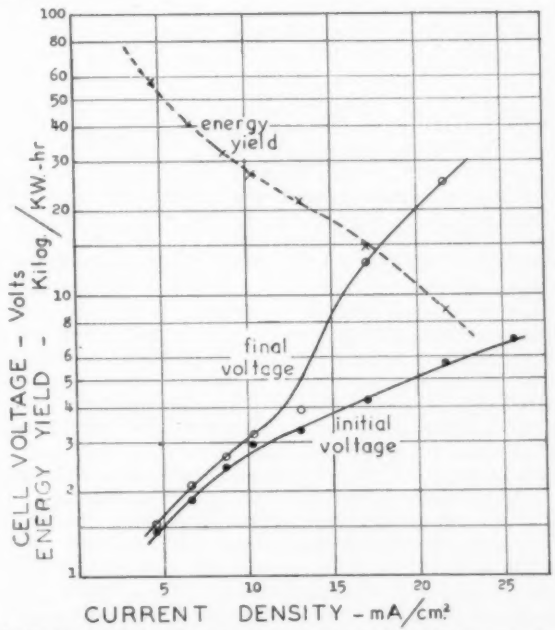


FIG. 3. Variation of cell voltage and energy yields with current density. For plating conditions, see Fig. 2.

Although the energy-yield curve shows a decrease of yield with increasing current density, it will be apparent that, even at higher current values, the yields are extremely high. From a practical standpoint, higher current density operation would be preferred, since the time saving would more than compensate for the added power cost, and plating is more uniform.

EFFECT OF DURATION OF DEPOSITION

Fig. 4 shows the variations in current yield and moisture content of electrodeposits with time of deposition at a constant current density. Both the current yield and moisture content of synthetic resin films decrease with increasing time of plating.

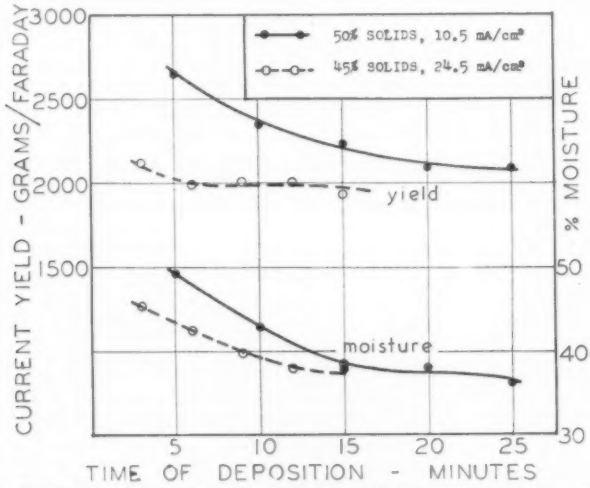


FIG. 4. Variation of current yield of Saran with time of deposition at constant current density.

Most authors, including Sheppard (42), have found that, in the case of rubber plating, yields increase linearly with time, or, in other words, that the deposition follows Faraday's law. Klein (25) gives a yield-time curve which deviates slightly from linearity, also showing a decreasing current yield with increasing plating time. This point will be considered later, when discussing the deposition mechanism.

It is readily appreciated why the moisture content should decrease with time. To give a numerical example, suppose that a 1 mm. thickness of polymer is deposited in 10 minutes and that this layer has a water content of 50 per cent. Continuing the plating for another 10 minutes applies another layer about 1 mm. thick and also having a moisture content of 50 per cent. But, meanwhile, the water content of the first layer has dropped below 50 per cent, so the over-all moisture content of the deposit is also below 50 per cent.

CHOICE OF ELECTRODE

The electrode material chosen for anode will greatly influence both the deposition process and the properties of the polymers after deposition.

Effect on electrodeposition

As far as the deposition process is concerned, there are two types of anodes: insoluble and soluble. An insoluble or passive electrode gasses (generally oxygen is evolved), so, highly porous and brittle film results, useless for most purposes. At very high current densities, almost any anode will start gassing, but insoluble anodes are, by definition, those electrode materials which will give rise to gas evolution at current densities normally used in synthetic resin plating. Aluminum, stainless steels, and carbon are such anodes. Lead starts gassing at about 10 milliamp./cm.^{2}, and, therefore, is not too useful as an electrode material.

A number of methods have been devised to solve the problems created by this gas evolution in rubber plating, and most of the methods are equally usable for synthetic resin latices. In one method, the polymer is deposited on a porous diaphragm interposed between anode and latex (26), as will be discussed later. Another method is to operate at very low potentials, below the decomposition voltage of water. The Williams process (53, 51) for rubber deposition is partly based on the latter, which takes a long time, and the deposit is not packed well enough.

Still another method involves an anodic depolarizer, that is, a substance that will be anodically oxidized below the potential at which oxygen evolution takes place. A number of such substances have been proposed (23, 30, 45): sulfur compounds, dyestuffs, phenolic amines, polyhydroxy phenols, and others. With resorcinol added to Saran latex, we were not able to suppress gassing completely at aluminum anodes. Another type of depolarizer is designed to promote regular solution of the anode and suppress passivation by forming complex ions with the solution products of the electrode: for example, the use of thiocyanates in conjunction with iron electrodes (41) was tried in our experiments with some measure of success.

When plating directly on an electrode, the gassing problem is most generally avoided by using a soluble anode (4): zinc, cadmium, iron and mild steel, tin, nickel, copper, etc. All of these have a range of current density over which uniform plating without gassing is possible. The range is largest for zinc, and is large enough for nickel and iron to make plating practical. The choice of an electrode will be largely determined by the relative properties of the polymer film after plating.

It was found that the yield per faraday, for a given number of faradays passed through the latex, not only is independent of the current density, but is the same with zinc, nickel, and iron anodes. For these three electrode materials, weight loss measurements showed that anode solution is practically quantitative. The same measurements also showed that, at the potentials used, iron dissolved in the ferrous form only. This can be borne out by visual observation: electrodeposits on iron freshly taken out of a plating bath are green; upon drying, the surface of the deposit turns brown (ferric), but the core of the material remains green for a considerable time, during which drying and diffusion of oxygen into the interior slowly proceed. Even more striking is the influence of thiocyanates

when incorporated in the latex: a deposit from a Saran latex containing dissolved NH_4SCN on iron will be light green when taken out of the bath (as in the case where no thiocyanate is present). During the drying process, the surface will turn deep red (color of the ferric complex), but a freshly cut surface exposing the core of the film will still be light green. It takes about two weeks for the deposit to turn deep red throughout. In the case of tin electrodes, measurements show that the anode goes into solution largely as Sn^{++} ions, but that some Sn^{++++} must also be formed. At the same time, the resin yield per faraday appears to be lower than on zinc, nickel, or iron electrodes.

Experimental results reveal that no electrode dissolution products get beyond the boundaries of the deposited layer. If a solution containing nickel ion is added to a latex containing dimethyl glyoxime, there is considerable thickening of the latex and a pink coloration appears because of the formation of the familiar nickel-dimethylglyoxime compound. It takes very little nickel ion to produce a perceptible pink coloration. Films cast from such a pink, thickened latex, after drying, stay pink for a month when kept at 85°C. When Saran was deposited on a nickel anode from a latex containing dimethyl glyoxime, no coloration or thickening of any kind was perceptible in the body of the suspension. At the same time, the electrodeposited layer had a very definite color that was no longer pink, but was the dark red-brown color of an oxidation product that can be reproduced by adding peroxide to a nickel solution being precipitated with glyoxime. The residual latex containing dimethyl glyoxime, after deposition on nickel, was dried, and a Saran film of the usual color was obtained, showing no pink spots.

In anodic deposition, a careful cleaning of the electrodes is not too important. Several successive deposits made on a zinc anode, without any intervening cleaning, all showed the same good properties. Generally, soap and water cleaning was sufficient.

Effect on properties of electrodeposits

When we consider the effects of electrode solution products on the properties of electrodeposited synthetic resin films, a number of electrodes are immediately eliminated. Thus, copper and copper alloys make all deposits from latex brittle and cause cracking during drying. Nickel proved to be an all-round satisfactory anode (unlike its performance in rubber deposition as reported in the literature (12), having a good plating range, and producing ions which interfere but little with the drying and curing of the deposits.

Iron electrodes introduce a different problem. It was pointed out above that iron enters solution in the ferrous form. As a portion of the ferrous ion in the deposit becomes oxidized to the ferric form, a certain amount of brittleness and shrinkage results and generally causes cracking. However, cracking is serious only in thick deposits. Thin films behave quite satisfactorily. The addition of thiocyanate to the latex was useful, not so much because it depolarized the iron anode, but because it ties up the ferric ions as they are formed after drying of the deposits, with a resulting improvement in the properties of the deposits.

Zinc and cadmium anodes have an excellent plating range and their ions

give a good combination of toughness and flexibility to electrodeposits of latex. Furthermore, zinc compounds have a very special effect on vinyl halide polymers that may be a serious limitation, and which will be discussed below. Lead and tin solution products, on the other hand, have a beneficial effect on the aging of vinyl electrodeposits.

TREATMENT OF ELECTRODEPOSITS AFTER PLATING

After deposition, the plated layer is a gel containing a considerable amount of liquid. It must be dried, either at room temperature or in an oven; it may require a wet cure before drying. For Saran deposits, an oven-drying period up to 30 minutes (depending upon the thickness) at 85°C. was found to be most satisfactory. After such a cure, the deposit can be handled mechanically, although not all of its moisture is removed as yet. After the heat treatment, it may take 2 to 3 weeks for the film to come to constant weight. A Saran electrodeposit may also be air-dried, but it is weak unless it is subsequently heat-treated at 85°C. for about 15 minutes. It is not advisable to go to temperatures higher than 85°C. with a dry deposit on account of the rather poor heat stability of the resin (especially when containing zinc). On the other hand, curing in boiling water does not destabilize the plastic.

Unplasticized Geon latex yields a deposit that has hardly any cohesion at all, and just crumbles if dried at room temperature. A heat-treatment at about 150°C. is needed to coalesce the deposit. At that temperature, destabilization and cracking takes place unless special precautions are taken. It is much more practical to use a plasticized latex. With plasticized vinyl chloride deposits, the best results are obtained by air-drying, followed by an oven cure at 85°C. If the deposit is oven-dried without preliminary air-drying, a pattern of small, localized cracks develops throughout the deposit without, however, causing complete fracture of the deposit. Geon electrodeposits on nickel appear to have better drying characteristics than those on zinc.

We had difficulty in finding curing conditions for styrene-butadiene copolymer, which develops a considerable number of cracks upon air-drying and especially upon oven-drying. It seems that, for best results, the copolymer electrodeposit, immediately after plating, should be cured in a water vapor atmosphere at or slightly below the boiling point of water; after such a cure, it may be air-dried. Even so, no satisfactory results are obtained unless the latex, whose pH is normally 8–9, is first acidified to a pH of 2–3.

It has been proposed in the patent literature (2, 46) to remove most of the moisture content of electrodeposits by electro-endosmosis. This is said to remove some of the water-soluble constituents along with the water, and possibly decrease the water-absorption of the deposits (32). It was attempted to subject some Saran deposits to 120 volts, making the electrode carrying the fresh deposit anode in tap water or in a NaCl solution. The moisture decrease was small, the water resistance of the deposits did not improve appreciably, but the tendency of the deposits to crack upon drying increased.

Electrodeposits obtained in our work were very readily stripped from the electrodes on which they were made. With a flat electrode covered on

both sides and the edges, it is generally possible to strip the whole deposit in one piece. Thus, double thickness resin sheets may be obtained in one operation.

HEAT STABILITY OF VINYL ELECTRODEPOSITS

None of the vinyl resins is too good in its heat resistance, yet they all can be kept at temperatures of about 100°C. for considerable periods of time. However, zinc compounds are known to reduce the heat stability of vinyl polymers very considerably (52), and this is especially true for electrodeposited vinyl and vinylidene chloride films, in which the distribution of zinc is very uniform. To a lesser extent, ferric ion has the same destabilizing effect, providing another good reason for adding thiocyanate to latex for deposition on iron. For example, if a sample of Saran that was electrodeposited on zinc is kept for 24 hours at 85°C., it is hardly recognizable, having turned completely black, becoming very stiff and no longer thermoplastic, yet remaining tough and not too brittle. It is merely swelled by vinyl solvents which disintegrate normal electrodeposits. If the sample is then immersed into one of these vinyl solvents, such as an ester for 24 hours, or into a ketone for a few hours, its properties change again; it becomes quite flexible, much softer, and even exhibits a small degree of rubber-like elasticity (rapid elastic recovery) that the original material (before heat-treating) never showed. In other words, the material now has some of the properties of vulcanized rubber.

The same effect is observable with polyvinyl chloride electrodeposits on zinc, when a "vulcanisate" with similar properties is obtained. On the other hand, when heat-treating a sample of styrene-butadiene copolymer for 24 hours at 100°C., only a slight amount of discoloration takes place, due to the oxidation of the partially unsaturated copolymer (this oxidation takes place whether zinc is present or not). The heat-vulcanization effect, then, is quite specific for vinyl halides.

The following explanation may be offered for the observations described above: the decomposition of vinyl halides takes place with the evolution of hydrogen halides and the formation of double bonds:

$$\underset{\text{polyvinylidene chloride}}{-CH_2CCl_2-CH_2CCl_2-} \xrightarrow[Zn^{++}]{\text{heat}} -CH_2\overset{Cl}{\overset{|}{C}}=CHCCl_2- + HCl \quad (I)$$

$$\underset{\text{polyvinyl chloride}}{-CH_2CHCl-CH_2CHCl-} \xrightarrow[Zn^{++}]{\text{HEAT}} -CH_2CH=CHCHCl- + HCl \quad (II)$$

These double bonds make possible the cross-linking of the linear vinyl chains, with the formation of insoluble, infusible polymers. Chain element (I) resulting from the decomposition of polyvinylidene chloride can be compared to the element $-CH_2\overset{Cl}{\overset{|}{C}}=CHCH_2-$ of a linear polychloroprene chain; chain element (II) resulting from the decomposition of a polyvinyl chloride may be likened to the element $-CH_2CH=CHCH_2-$ of a polybutadiene chain. Thus, it is not surprising that the decomposition prod-

ucts of polyvinyl halides show some rubberlike properties. Structurally, they resemble some of the synthetic rubbers. Now, although in the case of Saran latex, the acrylonitrile group in the copolymer may be a major factor in the cross-linking process, the vinylidene chloride part will also contribute considerably to the cross-linking under the above conditions. With Geon electrodeposits, the cross-linking is due wholly to the above mechanism. To show that it is the polymer itself which determines the heat-vulcanization characteristics and not other ingredients in the latices, we dissolved a sample of polyvinyl chloride[7] molding powder in cyclohexanone and added zinc chloride to one part of the solution. A film cast from the zinc bearing portion turned black rapidly when heat-treated, and was much stiffer than a film obtained from the unmodified portion, which stayed clear under the same conditions.

By subjecting Saran samples containing various ionic additions to the same heat treatment, it can be shown that zinc is quite unique as a "heat vulcanization" catalyst. On the other hand, samples containing nickel or especially lead ions show a good resistance to decomposition by heat: this should be compared with the fact that lead compounds are often used as vinyl stabilizers (52).

By varying the time and temperature of the heat treatment of electrodeposited latex films, any desired degree of vulcanization can be obtained: thus, we can make a controlled use of the phenomenon of heat destabilization of vinyls (considered exclusively as a "curse" up to now) to form useful products, comparable in many respects with those made of hard rubber.

INFLUENCE OF PH

With rubber latex, it is known that a decrease in pH will cause either coagulation of the latex, or even a reversal of the charge on the suspended particles if special precautions are taken (12). This reversal of charge is due to the protein component of rubber latex particles (20). It is explained most readily by the following equation, showing the effect of pH on the ionization of an amino acid:

$$^{+}NH_3RCOOH \xleftarrow{+H^+} \underset{\downarrow\uparrow}{NH_2RCOOH} \underset{}{} \xrightarrow{+OH^-} NH_3RCOO^- \quad (+H_2O)$$

$^{+}NH_3RCOOH$: Positive charge, Cathodic migration

NH_3RCOO^-: Negative charge, Anodic migration

Whether a change in pH has the same effect on the synthetic resin suspensions as it has on rubber latex depends upon the emulsifiers used in making up the suspensions, because the synthetic polymers we used do not contain any amino acid or similar amphoteric groupings. The negative latices used in this work contain anion-active agents, and no charge rever-

[7] Geon 101 Resin, The B. F. Goodrich Chemical Company.

sal was either expected or observed. Saran latex does not coagulate for a long time at pH values as low as 1, at which anodic deposition still is obtainable. With polyvinyl chloride latices, coagulation occurs at pH values of about 2, above which electrodeposition is strictly anodic. Butadiene-styrene latex does not coagulate at a pH of 2.

Besides affecting the sign and magnitude of the charge on suspended resin particles, low pH values have an unfavorable influence on the "throwing power" during electrodeposition (this may be due to increased conductivity). In the case of Saran and Geon latices, a high acidity adversely affects the aging characteristics of zinc-containing films. On the other hand, with butadiene-styrene copolymer as mentioned before, a low pH appears to be necessary for proper curing of the electrodeposits.

With vinyl acetate latices, in which emulsifying agents differ from those used in our negative latices (8), reversal of charge occurred (without coagulation) at pH values of about 9, obtained by the addition of ammonia, and a definite anodic deposit could be observed. This deposit would slide off the electrode as soon as it was lifted out of the bath. At low pH, a thin cathodic deposit was observed, especially if a salt (such as $AlCl_3$) containing a polyvalent cation was added. The addition of polyvalent cations to reverse the charge of rubber latex particles has been reported (24). All of the vinyl acetate deposits, however, whether anodic or cathodic, were useless for any practical purposes, being mechanically unstable.

If the negative latices are made alkaline by the addition of ammonia, sodium phosphates, or sodium hydroxide, the results are all unfavorable. Insoluble compounds are formed at the electrode surface, and electrode products do not diffuse through the deposit at the same rate as before. Thus, despite the increased conductivity of the main body of the latex, the resistance of the electrodeposit goes up considerably, and so does the overall resistance. The current yield decreases considerably. The uniform plating range decreases or may even disappear, and the deposits have a grainy structure with pinholes. Gassing sets in if the alkalinity is high enough, and the deposits show marked brittleness. For rubber deposition, a high alkalinity has also proved unfavorable (10).

CONCENTRATION EFFECTS

Most of the results reported so far are relative to undiluted latices. Fig. 5 shows the effect of latex concentration on the current yield and moisture content of Saran electrodeposits. It is seen that, down to 30 per cent concentration, the current yield decreases but little with increasing dilution, but the moisture content goes up rapidly, so that, at 20 per cent solids, we were unable, at normal current densities, to obtain a deposit that would adhere to the electrode when taken out of the plating bath. To get an adherent deposit from 20 per cent Saran latex required a current density of 80 milliamp./cm.^{2} at which plating from a more concentrated suspension is impossible. At 80 milliamp./cm.^{2} the deposit, when withdrawn from the bath, was steaming hot, and this heat was probably what had given the deposit a little mechanical strength. However, the moisture content was still so high that liquid oozed out and dripped from the deposit for a long time, which was never observed with deposits from more concentrated latex baths.

This variation of current yield with concentration is contrary to all of the results previously reported for rubber deposition. Sheppard (42) indicates a direct proportionality between current yields and concentration. Mathieu (35) reports a threefold increase in current yields when the concentration of rubber latex is increased from 30 per cent to 54 per cent. Our results are somewhat closer to those of Klein (25), who found that the current yield increases as the square root of the concentration.

This situation was investigated further with polyvinyl chloride latex, from which it is possible to get coherent and adherent deposits even at latex

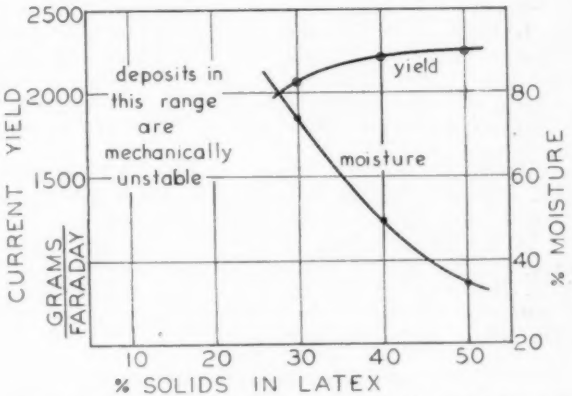


FIG. 5. Effect of latex concentration on current yields and moisture content (per cent of dry deposit weight) of Saran electrodeposits. Current density and plating time were held constant.

TABLE II

Concentration of latex (% solids by wt.)	Size of latex sample	Grams of solids in latex sample	Yield in grams	Grams per faraday	Time of deposition
%					*minutes*
40	63 ml. = 71 g.	28.4	14.40	3090	15
30	63 ml. = 69 g.	20.7	11.56	2500	15
20	63 ml. = 67 g.	13.4	9.13	1970	15
10	63 ml. = 65 g.	6.5	5.95	1290	15
10	63 ml. = 65 g.	6.5	2.80	2250	4

concentrations as low as 10 per cent. Comparatively small samples were used, so that the solids content was exhausted at a rapid rate. The results are reported in Table II.

With 20 per cent and 10 per cent concentrations, the liquid remaining in the latex compartment after deposition was very dilute; with 10 per cent latex, it was almost clear. When taken out of the bath, the apparent volume occupied by all of the 15-minute deposits was about the same; if anything, the deposit from the 10 per cent latex seemed to be bulkier. The

15-minute deposit from 10 per cent latex started "bleeding" liquid rapidly, the 20 per cent latex deposit more slowly.

The data in Table II show that, even in this case, the yield—concentration relationship is far from being linear. Also, exhaustion of the suspensions affects the results: exhaustion is practically complete when passing current for 15 minutes through 10 per cent latex. When passing current for only 4 minutes through the same 10 per cent latex, the current yield *goes up by a factor of 75 per cent.* This is quite a deviation from Faraday's law, and is inconsistent with other results for rubber and synthetic resin deposition (obtained under constant concentration conditions). In other words, if it was not for depletion, the current yield from a 10 per cent Geon latex might be expected to be about 2250 grams/faraday if not higher, since this figure of 2250 grams/faraday is already affected by a depletion of nearly 45 per cent. From the results obtained with Saran as well as those with Geon latex, we may conclude that, while the current yield decreases with decreasing concentration of latex, the yield is far from being proportional to the concentration of latex.

In order to make a fair comparison of our results with the relations between yields and concentration reported for rubber, one would have to know the exact experimental conditions under which the investigations with rubber latex were carried out: the size of sample used, length of time of deposition, and whether the rubber latex was concentrated by centrifugal methods (this would change the proportions of the current carried by colloid particles and ions). We shall return to this question in our consideration of the deposition mechanism.

ELECTRODEPOSITION ON DIAPHRAGMS

As mentioned above, it may be desirable to get away from electrode products (such as gases interfering with the deposition or ions interfering with the properties of the deposits). In such cases, an anodic diaphragm, interposed between anode and latex, has been used for rubber deposition (3, 25, 26). These diaphragms can be fabricated to the shape and size that is desired for the finished rubber goods. It was tried to apply the same principle to our negative synthetic resin latices. By far the best results, from a standpoint of uniformity of deposits as well as yields, were obtained by filling the inside of a porous cup diaphragm with mercury (which was made anode), the diaphragm having been soaked in a salt solution (sodium chloride or sodium acetate). The mercury compounds formed are insoluble or very little ionized, and stay inside the porous cup. The resistance of the anodic film increases rapidly, the potential likewise goes up very rapidly from about 3–5 volts to values of about 40–70 volts, and it is not possible to maintain the initial current density.

Current yields were found to be comparable with those obtained on soluble electrodes, being mostly lower for Saran and higher for Geon deposits, and not being too readily reproducible. Typical current yields were 1600 grams/faraday for Saran and for styrene-butadiene copolymer deposits; Geon yields ranged from 3600 to 4500 grams/faraday. Energy yields, of course, were much lower than in the case of direct deposition on electrodes, due to the higher voltages used: the order of magnitude was 3 or 4 kilograms/kw.-hr. The mercury would get very warm during the deposition.

Initial current densities were about 5 milliamp./cm.^{2} of outer diaphragm surface, and plating times did not exceed 10 minutes. Thicknesses up to 1 mm. were built up.

The deposits are readily stripped from the diaphragms, after an appropriate heat treatment. Since no electrode products are incorporated in the deposits, the temperature can exceed 85°C. for short drying periods, if desired. It was found best to subject the deposits to air-drying first, followed by a curing period of about 15 minutes at 85°–100°C. Electrodeposits made from a mixture of Geon and styrene-butadiene latices strip particularly readily.

For thin films, electrodeposition on a porous form has little advantage over dipping the same form into the latex, followed by drying, curing, and stripping. However, as soon as any thickness is desired, electrodeposition means a time saving and a more uniform deposit.

Both porous clay and alundum diaphragms were used. For deposition from synthetic resin latices, it did not seem to make much difference which one was used.

All the experimental runs were made at room temperature. The first reason for this is that the latices have a maximum stability at room temperature, being sensitive to freezing on the one hand, and on the other hand more or less subject to coagulation at high temperatures. Furthermore, coagulation takes place at the anode, where the local temperature or energy level is quite different from that in the bulk of the suspension. It was pointed out above that charring of an electrodeposit may take place at the anode when still in the bath, while the bulk of the latex is almost at room temperature. The existence of such a high energy level at the anode surface has been reported in the literature, in particular by Fichter (15) who indicates that, in electroorganic anodic reactions, at room temperature, we get compounds which are formed only at high temperatures when prepared chemically.

Whenever circulation was used, it was very mild, about 3 per cent of the cell contents per minute. At higher rates of circulation, frothing of the latices will start, with decided disadvantages which far outweigh any benefits to be derived from a faster circulation.

OPTIMUM CONDITIONS FOR SARAN PLATING

The following optimum conditions are indicated for Saran electrodeposition:

1. Current density: 15–20 milliamp./cm.^{2}
2. Total cell voltage: 3–5 volts (will vary with type of cell), including the potential drop across a low resistance cathodic diaphragm.
3. Saran latex containing about 50 per cent solids in anode compartment.
4. Dilute NaCl solution (about 5 per cent) in cathode compartment.
5. A mild circulation of the latex is recommended (about 3 to 6 per cent of the cell contents per minute).
6. Recommended soluble anodes: nickel or cadmium if good aging characteristics and heat stability are desired; zinc if the stiffening and discoloration upon aging are not important, or if it is desired to heat-vulcanize the material after deposition. Iron and mild steel are also satisfactory as

anodes, especially if a thiocyanate is added to Saran latex before plating. Color possibilities, however, are restricted in this case.

7. Immediately after deposition, a heat treatment at 85°C. is recommended: its duration varies with deposit thickness, but should not exceed 30 minutes.

THE MECHANISM OF ANODIC DEPOSITION

A number of theories have been proposed for the deposition of rubber (3, 19, 42), but not much of an attempt has been made to correlate all of the experimental data and facts with these theories.

Sheppard (42) pointed out that, when an electric field is applied to a colloidal suspension also containing dissolved salts such as NaCl, there is no essential difference between the behavior of colloids or ions as far as conduction and migration is concerned. If we can carry this analogy one step further, and state that electrode reactions, whether involving colloids or ions, proceed at a definite electrode potential or energy level, and that two simultaneous electrode reactions, whether involving colloids or ions, are possible only if the potentials at which they take place are the same, we are then in a position to show that the deposition of synthetic resins can hardly be the result of a *direct discharge* of the negative charge of polymer particles at the anode (see below).

Coagulation by cations

The deposition at the anode of synthetic resins from latices may have as its controlling step either the migration of the suspended particles toward the anode, or else a reaction initiated at the anode.

The idea that zinc ions generated at the anode are the chief agents in the electrodeposition of rubber was most explicitly stated by Beal (3), who also realized that the migration velocity of zinc ions through the layer of rubber already deposited has a bearing on the growth of the deposit. However, Beal's theory was qualitative and unsupported by any experimental evidence.

All the present experimental data point to the fact, at least in the case of deposition from synthetic resin latices, that the anodic process is the controlling one. In the case of soluble anodes, the ions produced by electrode solution (Zn^{++}, Fe^{++}, Ni^{++}) seem to do the coagulating. As supporting evidence, it was shown that no cations produced at the anode migrate beyond the boundaries of the electrodeposit at the anode which coincides with the furthest point of travel of the ions. It is this coagulation, combined with electro-osmotic and ionic dehydration of the deposits, that yields thick, adherent, and coherent layers at the anode.

If every cation created by anode solution *and coming in contact with the latex* contributes to the coagulation of resin particles, there should be a definite ratio between a given number of ions and the number of colloid particles coagulated by those ions. The fact that Faraday's law is approximately applicable to the electrodeposition from latices, and the fact that the same yields are obtained whether we used iron, nickel, or zinc anodes, seem to confirm that such a ratio exists.

Calling R the weight of resin (dry basis) that will be coagulated by one equivalent weight of divalent cation (Zn, Ni, Fe), the weight yield of the resin is

$W = R \times$ the number of equivalents of cation that has effectively arrived at the latex-electrodeposit interface, and, therefore, has taken part in coagulation.

I amperes passed for t minutes through the suspension, produces a deposit of thickness of T cm. (including the water content) containing W grams of dry resin. If v is the average migration velocity of the cations (in cm./min.), the following relations exist:

After t minutes of deposition, consider those cations which have just reached the present boundary between latex and coagulated layer, and are on the verge of participating in further coagulation. Any cations formed at the anode after the above ions were formed are still traveling inside the coagulated layer and have not taken part in the coagulating process. It has taken the cations which have just reached the boundary $\frac{T}{v}$ minutes to travel from the electrode surface to this boundary. During those $\frac{T}{v}$ minutes, there is anodic solution of

$$\frac{60 \times I}{96{,}500} \times \frac{T}{v} \text{ gram-equivalents of electrode (or cation).}$$

The total amount of cation formed since the beginning of the deposition (at 100 per cent anodic efficiency) is

$$\frac{60 \times I \times t}{96{,}500} \text{ gram-equivalents,}$$

and, therefore, the amount of cation having participated in the coagulation is

$$\frac{60}{96{,}500}\left(I \times t - \frac{I}{v} \times T\right) \text{ gram-equivalents,}$$

and W = dry weight yield $= R \times \frac{60}{96{,}500}\left(I \times t - \frac{I}{v} \times T\right)$ grams (*Equation A*).

Let us now compare the experimental data with the above relation. First of all, consider what happens when a constant number of coulombs is passed through the suspension. The product $I \times t$ remains constant and $\frac{I}{v}$ will also be practically constant. As long as moderate current densities are maintained, all deposits have approximately the same ohmic resistance, which means that the ionic migration velocity will be proportional to the potential across the deposited layer, which, itself, will be proportional to current. Consequently, equation (A) above predicts that the weight deposited will be constant, which is confirmed by experimental observation (Fig. 3).

Next, consider the time-yield curves. According to Fig. 4, the current yield decreased slightly with increasing time of deposition. The migration velocity of the cation through the coagulated layer will depend upon the mechanical resistance and the water content of the deposit. As long as the deposit is fairly loosely packed, or high in moisture, a certain amount of electro-osmotic dehydration (and simultaneous decrease of the thickness T) will have little effect on the resistance to migration and on the migration velocity v. But, a stage will be reached when more dehydration (without causing much change in the deposit thickness T) will considerably slow down the migrating ions. We have seen that the electro-osmotic dehydration is not uniform, but that most of it takes place in the layers adjacent to the anode surface, which is where the cations will be slowed down. If, at constant current, the plating time is doubled, the term $I \times t$ of equation (A) is doubled, the thickness T is almost (but not quite) doubled, but, on the other hand, the velocity v (which is an average velocity) decreases appreciably. Consequently, the term $\frac{I}{v} \times T$ is more than doubled, and the weight yield per faraday decreases somewhat. It was pointed out that more dilute latices lead to deposits with a higher water content. According to the above discussion, then, electro-osmotic dehydration of these high moisture deposits should not cause too much of a drop in the migration velocity of the coagulating cations, and, consequently, the rate of decrease of current yield with deposition time should be less rapid for more dilute latices than for more concentrated ones. A look at Fig. 4 will confirm this prediction. At 45 per cent concentration, the time-yield relationship is almost linear, and Faraday's law is obeyed. Actually, keeping the above correction for migration velocity in mind, we may state that *the deposition of synthetic resins from their latices follows Faraday's law in all cases.*

It is unfortunate that we do not know and cannot determine the actual values of the migration velocity v inside the coagulated gel. However, we can get at least an order of magnitude: the mobility of zinc ions is about 5×10^{-4} cm./sec. per volt/cm. in aqueous electrolyte solutions. With fairly loose packing of the deposits, assume that it is about 3×10^{-4} cm./sec. per volt/cm. inside the coagulated layer. In one experiment, 0.75 ampere was passed for 24 minutes through the suspension, building up a deposit about 0.3 cm. thick containing about 25 grams of dry resin on a zinc anode, with a potential gradient across the deposit of about 1 volt/cm. Then the migration velocity of the zinc ions is of the order of 3×10^{-4} cm./sec. or 2×10^{-2} cm./min. The term

$$\frac{I}{v} \times T = \frac{0.75}{2 \times 10^{-2}} \times 0.3 = 11,$$

while the term $I \times t = 0.75 \times 24 = 18$.

Thus, the number of cations remaining in the coagulated deposit and not participating in the coagulation process may be a very substantial fraction of the total number generated at the anode.

Substituting the values of the above numerical example in equation (A) gives a value of 5900 for the factor R. This means that 1 gram-equivalent

of divalent ion (note that the yields per faraday for zinc, iron, or nickel were the same) will coagulate 5900 grams of (dry) Saran from its latex. If we assume that the positive charges of the ions will completely neutralize the negative charge of the colloid, we can get an idea of the charge on a latex particle. Assume that we are dealing with spherical particles with an average size of 0.1 μ (it ranges from 0.08 to 0.15 μ). The specific gravity of the solid phase is about 1.55. Then the average weight of a particle is

$$\frac{\pi}{6} \times 10^{-15} \times 1.55 \text{ g.}$$

and the number of particles coagulated per gram equivalent of divalent ion is

$$\frac{6 \times 5900}{\pi \times 1.55 \times 10^{-15}} = 7.3 \times 10^{18}.$$

But 1 gram equivalent of ions carries 6.0×10^{23} electron charges; therefore, the number of charges per particle is about

$$\frac{6.0 \times 10^{23}}{7.3 \times 10^{18}} = 8 \times 10^{4} \text{ electron charges.}$$

Actually, it is not certain whether all the charges on the latex particles are neutralized by zinc ions, so that the above value gives an order of magnitude only of the charge on the colloid.

Next consider the effect of concentration on yields. It was shown before that the moisture content of deposits from dilute latices increases rapidly with the degree of dilution. The coagulation of a portion of latex "freezes" its liquid component in place, until it starts to be removed by electro-osmosis and by ions; the more dilute the latex, the greater the amount of liquid that is thus incorporated in the gel; and, for a certain number of coulombs passed through a suspension, the thickness of the wet coagulated layer increases considerably as the dilution of the latex is increased. This fact is amply confirmed by experimental observation. As a result of which, the cations have to travel much further before reaching the boundary of the coagulated layer. Therefore, a smaller proportion of the ions generated at the anode will actually partake in the coagulation of the latex (even though the migration velocity v is slightly greater in a loose deposit). This accounts for the decrease in yields observed with decreasing concentrations of polymer suspensions. On account of electro-osmosis and transport of water by ions, it is not possible to determine exactly how much the thickness T will change with latex concentration, so, a quantitative relationship between concentration and yield cannot be predicted. An inspection of equation (A) shows that there is no simple proportionality between concentration and current yield.

The migration velocities of zinc, ferrous, and nickel ions are all of the same order of magnitude: equation (A) then accounts for the fact that, for a given number of coulombs passed through a latex under similar conditions, the yield of electrodeposit is about the same with an iron, zinc, or nickel anode.

It should be emphasized that ionic coagulation by itself would be insufficient to produce serviceable deposits. Coagulation has to be helped by electro-osmotic dehydration, and by the positive ions carrying away some of the water. Without this dehydration, no coherent deposits are obtained; and, in the case of Saran plates, when the moisture content of deposits from dilute latex becomes too high to be sufficiently removed by osmosis, the deposits collapse. We believe that the anodic energy level may also have a bearing on the formation of good deposits.

The nature of the coagulating effect of cations does not seem to be the same in the case of synthetic latices as in the case of rubber latex. Workers in the field of rubber deposition have attributed the negative charge of rubber particles to an adsorption of OH^- ions (19), and claim that Zn^{++} or H^+ ions combine with these hydroxyls to coagulate the particles. In synthetic resin latices, the negative charge apparently is due to an adsorption of the anion part of the emulsifier keeping the particles in suspension, such as the fatty acid chain of a soap or the organic group of a sodium alkyl or aryl sulfonate. Zinc or nickel ions, which form water-insoluble compounds with soaps, could reasonably be expected to coagulate latices made up with such emulsifiers. Hydrogen ions in sufficient concentration have the same effect: they repress the ionization of the weak acids of which the active radicals of the emulsifiers are the anions (49):

$$(\text{Colloid} - R)\text{COO}^- + \text{H}^+ = (\text{Colloid} - R)\text{COOH}$$

It should be noted that H^+ ion or polyvalent cations, when added *directly* to synthetic latices in sufficient concentrations, will produce coagulation. On the other hand, cations of the alkali metals, which do not form insoluble compounds with the emulsifiers, may be added to synthetic latices in large concentrations without producing any coagulation at all.

In the case of deposition on diaphragms, the coagulation seems to be caused by the formation of hydrogen ions at the mercury anode. Although the pH of Geon latex is above 8, the pH of a deposit from this latex on a diaphragm is below 5. The fact that Geon yields are, if anything, higher on diaphragms than on soluble electrodes, whereas Saran and styrene-butadiene yields are lower, should be compared with the fact that Geon latex starts coagulating at a pH of 2, at which Saran and styrene-butadiene latices are still quite stable. In other words, it requires more hydrogen ion to coagulate the last two latices.

At the mercury anode, a number of *successive* electrode reactions are possible, due to the rapid rise in potential: at the lowest starting voltage, with a diaphragm that has been soaked in a NaCl solution, calomel appears to be formed, but the available chloride ion is rapidly exhausted, and the potential rises to a point where hydroxyl ions begin discharging. The voltages are probably high enough so that first mercurous and then mercuric compounds are formed. This possibility of multiple reactions probably accounts for the erratic current yields.

The effect of alkalinity gives further support to the theory that coagulation by cations is the controlling step in the electrodeposition of synthetic resins. If the alkalinity increases, the zinc ions formed at the anode will be partly precipitated as zinc hydroxide, or they may even form the *negative* $Zn(OH)_4^=$ complex. As a result, the number of zinc ions available for coagulation of the deposit and, consequently, the current yields would be expected to decrease with increasing alkalinity. This is confirmed by experiment.

Concentration of latex by electro-osmosis and electrophoresis

We have shown that the anodic coagulation caused by cations accounts for all of our experimental observations. However, we have found that it is possible to obtain very thin anodic deposits without the generation of cations taking place at the anode. Thus, if we apply a potential below the decomposition potential of water, between two similar electrodes immersed in a latex and insoluble therein (platinum or aluminum), for about 1 hour, at the end of this time we will observe a thin anodic layer and a thinning of the latex in the cathode region (no cathodic diaphragm was used in this test). This layer or deposit however, is *creamy* and uneven, and does not exhibit the firm, gel-like structure of electrodeposits on soluble anodes. The deposit observed here is uniquely due to concentration of the latex in the anode region by electrophoresis of the latex particles and electro-osmosis of water in the opposite direction. The deposited layer can be redispersed in dilute latex by simple shaking.

Biguenet (5) has recently proposed a theory for the formation of electrophoretic deposits, based on his work with positive alkaline earth carbonate suspensions. He considers, on the one hand, the repulsive forces between the charged suspended particles, which obey Coulomb's inverse square law:

$$F = -\frac{q^2}{r^2}$$

where q is the charge on each particle and r the distance between them. These Coulomb forces are appreciable at distances between particles of the order of several particle diameters. On the other hand, there are attractive forces (such as Van der Waals' forces) which become effective only when the distance between particles is of the order of their diameter. In dilute suspensions, the particle spacing is large, and the repulsive forces prevail. But, as we reach a certain critical concentration, the attractive forces start to overcome the electrostatic repulsion, and agglomeration results. The relative magnitudes of particle charges and attractive forces determine this critical concentration. In the case of latices, the emulsifying agent will be the factor determining the balance of forces and the critical concentration.

The above theory is quite satisfactory in explaining the formation of thin, creamy deposits from negative latices below the decomposition voltage of water. It also explains the formation of cathodic deposits from vinyl acetate latex containing Al^{+++} ions.

At this point, it is well to emphasize a very important distinction: the formation of anodic films from negative latices below the decomposition potential of water is due only to *concentration by electrophoresis and electro-osmosis, and not to the anodic discharge of charged ions or colloids.* Actually, the anodic discharge of a colloid particle probably would require a very high potential: it would mean the anodic oxidation of the emulsifier anion. If the anion is an alkyl sulfate, the potential required would be of the order of the oxidation potential of sulfate to persulfate; if the anion is an organic acid radical, the discharge potential would be the formation potential of the corresponding peroxide:

$$2\ R\text{—}COO^- - 2e = (RCO)_2O_2.$$

In most cases, another anodic reaction, such as electrode solution or hydroxyl ion discharge can and will take place at a lower potential than the above.

In the case of rubber latex, it may be that, at the anode, agglomeration due to concentration takes place along with coagulation by cations generated at the anode. This would help to explain the fact that in rubber deposition (35) the current yield may increase by a factor of 3 as the rubber content of the suspension goes up from 30 per cent to 54 per cent. Here, we are no longer dealing with a reaction that is controlled by the generation of cations at the anode. We might note that, if electrophoresis and electro-osmosis were the determining factors in electrodeposition from rubber latex, then, at a given potential, the yield for a given length of time would be proportional to the concentration of latex, as reported by Sheppard (42).

In the case of deposition from synthetic resins on a soluble electrode or on a diaphragm, however, the agglomeration by concentration will not have played too important a role, as shown by the following facts. Geon electrodeposits from latex whose concentration is below 20 per cent contain over 100 per cent water; that is, their solids content is smaller than that of the original concentrated latex (over 50 per cent), yet these deposits are coherent gels, whereas 50 per cent latex is a low viscosity suspension. Hence, we conclude that we must be dealing with coagulation of resin particles by cations; the material constituting the coagulated layer is not exactly the same compound as the resin dispersed in the latex: it differs by the presence of hydrogen or metal cations.

If the anodic deposition is controlled by coagulation by cations, the concentration by electrophoresis and electro-osmosis should not cause great variations in current yield at high latex concentrations. In the case of the synthetic resin latices, this is confirmed experimentally.

Oxidation reactions:

The fact that oxidation reactions forming peroxides occur at anodes has already been mentioned by Sheppard (42) and abundantly illustrated by Fichter (15). The possibility of peroxide formation during anodic deposition of synthetic resins should be considered, assuming the anode potential is high enough for a peroxide reaction to take place. If any peroxide products are formed anodically, they will give rise to free radicals which are well-known polymerization catalysts.

To determine whether or not anodic deposition is accompanied by polymerization, we tried to make a few viscosity measurements. We made up cyclohexanone solutions of (a) a Saran electrodeposit on nickel; and (b) a film cast from Saran latex, to which nickel ion had been added in the same concentration as in the electrodeposit. Both solutions were of the same concentration and were heated up the same length of time to effect solution of the resin. The results were inconclusive, as it was impossible to obtain perfectly clear solutions. The viscosity of the electrodeposit solution (capillary method) was about 22 per cent higher than that of the cast film. It may be that the anode potential was not high enough for peroxide formation.

To obtain more information on possible polymerization we tried to determine whether the passage of current would cause selective anodic polymerization of a monomer dissolved or suspended in a liquid. We first tried to disperse monomeric styrene in a water solution of potassium sulfate, and apply a d.c. voltage to the emulsion, using a platinum anode. Application of an electric field broke up the emulsions very rapidly, with a

concentration of all the styrene phase at the anode. Some polymerization could be detected, but could not be specifically attributed to the anodic action. Some oxidation of styrene to benzaldehyde was also noticed, as reported by Fichter (15).

Next an electric field was applied to an organic solution of styrene plus sodium benzoate, using a mixture of trichlorethylene and alcohol as the solvent phase. Unfortunately, the conductivity was very low, so that it would take about 24 hours to notice any change at all. (Attempts to increase the conductivity by the addition of inorganic salts or water resulted only in the breakup of the system into two phases). At the close of the experiment, the anode-compartment liquor had turned yellow, while the liquid on the cathode side of a porous diaphragm remained colorless. Upon evaporation of samples from both anode and cathode compartments, a small amount of a sticky, resinous residue was obtained from the anode compartment, but not from the cathode chamber. Thus, it was shown that an anode-induced polymerization is possible. However, we have no way of telling whether the anodic action consisted in the generation of free radicals, or in the oxidation of inhibitors that are always present in the monomer, or both.

PROPERTIES OF THE ELECTRODEPOSITS

Saran electrodeposits, after a short heat-treatment, are dark yellow to brown if deposited on a diaphragm or on a zinc electrode. Nickel or iron ions add their own color. They are opaque in all but thin sections. Zinc bearing deposits kept at room temperature slowly turn darker, until, after about 8 months, they become brown. Thinner deposits become less discolored than thicker ones.

The Saran films we produced are comparatively tough, but still quite flexible. They exhibit a visco-elastic behavior when stretched. Their elastic recovery is slow and incomplete for all but the smallest amounts of stretching. As the deposits age, their stiffness and strength increases somewhat, while their elasticity decreases. Nickel bearing Saran films age but little.

Tensile strength tests were made with Saran electrodeposits about 2 to 2.5 mm. thick and 13 mm. wide; the load was applied at a rate of about 100 lb./in.^{2}/min. (7 kg./cm.^{2}/min.). It was not feasible to maintain the available testing equipment under standard and constant conditions of temperature and humidity; consequently, the variation in the readings recorded was considerable. The tensile strength of Saran electrodeposits on zinc, 30 days after deposition, ranged from 690 to 830 lb./in.^{2} (49 to 59 kg./cm.^{2}), averaging about 750 lb./in.^{2} (53 kg./cm.^{2}) (on the basis of the initial cross-section area). The elongation was from 200 per cent to 230 per cent of the initial gage length. For comparison purposes, the tensile strength data reported in the literature (47) for Saran film cast from latex were obtained with films 0.002 in. (0.05 mm.) thick: the strength is reported as 2800 lb./in.^{2} and the elongation 220 per cent. It is well known that very thin films always give considerably higher tensile strength values. The tensile strength of the zinc-containing electrodeposits might have been improved, had it been possible to heat-treat them at higher temperatures without danger of decomposition.

Heat-vulcanized Saran electrodeposits were also tested. By varying the time of heat-treatment of zinc bearing deposits, the tensile strength and elongation could be varied, as shown in Table III.

Polyvinyl chloride deposits from plasticized latex are translucent to transparent, colorless to slightly yellow, with nickel and iron ions again imparting their specific color to the films. The best resistance to aging is shown by nickel-containing electrodeposits. Films deposited on zinc will gradually darken when kept at room temperature for 8 months. The deposits are softer, more elastic, and less tough than Saran films plated under the same conditions.

The styrene-butadiene copolymer deposits are also translucent and colorless at first, but they turn slightly yellow with aging. With time, this unsaturated polymer becomes oxidized and loses flexibility and elasticity. The latex was developed by its manufacturer primarily for air-hardening, as a component of various paint and coating formulations (11), and, therefore, is not too good for electrodeposits that are to be stripped and self-supporting. (The manufacturer makes another form of this latex,[3] which contains an antioxidant; but there is some question whether this modified form would be any better for electrodeposition purposes, as the antioxidant might be anodically oxidized). Codeposits of Saran and styrene-butadiene, on the other hand, show good aging properties and an improved elasticity over that of plain Saran films.

TABLE III

Time of heat treatment at 85°C.	Tensile Strength		Per cent elongation
	lb./in.^{2}	kg./cm.^{2}	
6 hr.	950	67	200%
12 hr.	1770	124	50 approx.
48 hr.	2020	142	10

One disadvantage of films made from synthetic resin latices, whether cast or electrodeposited, is that they still contain some water-soluble matter, and will have a higher water absorption factor than heat-molded or solvent cast films. This water absorption, however, does not seem to affect the physical properties much. Deposits immersed in water get milky white, and their flexibility is somewhat impaired. Aging improves the water resistance, but even heat-vulcanized films absorb water to a certain extent. Resistance to inorganic and organic chemicals is of the same order as that of molded or solvent cast sheets. Polyvinyl and polyvinylidene chlorides are well known for their excellent over-all resistance to chemicals.

SUGGESTED APPLICATIONS

The applications of the electrodeposition of synthetic resins are, generally speaking, the same as those of rubber deposition: electroforming of polymer sheets or articles directly (34, 48), without the use of special molding equipment or rolls; electric insulation (1, 46), protection of metals against corrosion and abrasion, etc. The equipment required is very simple, and

[3] Dow Latex 513, The Dow Chemical Company, Midland, Michigan.

power consumption for synthetic resins is even lower than for rubber plating. One distinct advantage of working with synthetic resin latices is that most synthetics are much more resistant to anodic oxidation than rubber. The manufacturers of synthetic resin latices supply directions for compounding their products with fillers, pigments, plasticizers, etc. (11, 21, 47): most of these are added to the latices in emulsion form. During electrodeposition these compounds will come out at the anode along with the polymers. The heat-treating temperatures for electrodeposits are below those required for molding and calendering of the synthetic resin latices. The versatility of the electrochemical method is increased by the fact that we can use anodic diaphragms of any desired shape or size, tie up some objectionable electrode products in complexes, change the surface finish of the deposits by varying the current density, and heat-vulcanize zinc-bearing deposits.

SUMMARY AND CONCLUSIONS

1. From commercially available synthetic resin latices containing negatively charged polymer particles, it is possible to obtain anodic deposits of considerable thickness with good physical and chemical properties, without needing to change the basic composition of the latex before plating.

2. The potentials needed to produce electrodeposits are considerably lower than those in rubber deposition. Current yields are of the same order of magnitude as for rubber plating; energy yields are much higher.

3. The electrode materials suitable for high polymer deposition are, on the whole, the same as those for rubber plating. However, the preferred electrode material may not be the same, because electrode products affect the properties of a synthetic polymer in a different manner than those of rubber.

4. All experimental evidence indicates that the controlling step in the electrodeposition of synthetic resins from latices is the anodic generation of cations (hydrogen and/or metal ions), rather than the electrophoretic migration of resin particles. The electrodeposition obeys Faraday's law.

5. By a suitable choice of anode material and of heat treatment, deposits may be obtained that are either soft, flexible and elastic, or tough and stiff, comparable with hard rubber.

6. The method requires very little special equipment and lends itself to a great number of variations.

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THE EFFECT OF IONIC ADDITION AGENTS ON THE POLARIZATION OF ELECTRODEPOSITION OF COPPER[1]

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ABSTRACT

Cathode potentials were measured by a modification of the direct method during the electrodeposition of copper on smooth platinum from a cupric nitrate solution. Various inorganic salts and acids were added to the simple bath and the resulting effect on cathode potentials noted. In certain cases where more than one concentration of an addition agent was used, maxima and minima of polarization were observed. The effect of the addition agents on the surface appearance of the plate was also noted.

INTRODUCTION

Metal addition agents have found rather wide use in industry as brighteners in commercial plating solutions. However, few comprehensive researches of a fundamental nature have been reported in this field.

Meyer and Phillips (1) made an electrochemical and crystallographic study of the effects of a number of foreign metal ions upon electrodeposition from a cuprocyanide bath. This bath is used commercially to obtain a smooth compact plate. Lead was the only ion used which effectively brightened the copper deposit. Where there was an increase in brightness there was also an increase in cathode polarization. Conversely, depolarization was coincident with a larger crystal size in the plate. They also found that some of those cations that did not codeposit had a decided effect on the structure of the plate and on the cathode polarization.

In addition to the interference effect of the foreign cations on the crystal growth of the deposit, either by substitutional or interstitial entry into the lattice, Meyer and Phillips list the following variables introduced by the cation which may alter the structure of the plate:

"1. Precipitation of the foreign metal ion in the cathode film as a basic salt or other compound, followed by inclusion in the metal lattice.
2. Cathode polarization.
3. Cathode efficiency.
4. Hydrogen overvoltage on the parent metal or alloy."

Taft (2) concluded that there are at least two ways for addition agents

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to affect the deposit. One type of agent is readily adsorbed and is included in the deposit. Such agents as gelatin act in this manner. A second type of addition agent is reduced at the cathode simultaneously with the metal ion. This type of agent has not been found in the deposit. Nitrate ions are reduced at a copper cathode and act as an addition agent in an acid copper sulfate bath. The onset of a second cathodic process such as this may be an explanation of a slower increase in cathode polarization at the higher current densities than at the lower.

A third type which must be considered is the agent which is reduced at the cathode and included in the deposit. Those metallic ions which are codeposited are placed in this class.

Much work has been done on beneficial organic and colloidal addition agents. The main general conclusions drawn are that these agents induce a finer grained deposit and that they increase polarization in the process. Data hitherto available indicate that inorganic addition agents give results in accord with these conclusions.

APPARATUS

For the current densities used in this work, the direct method of measuring cathode potentials gives results which are probably as accurate as those of the commutator method. When, as in this work, it is desired to study the change in polarization on the addition of an acid or salt, the difference in the results obtained by the two methods becomes of negligible importance. Since the direct method is the simpler, it was chosen.

Twinned circuits were used (see Fig. 1.). The use of the two identical circuits rather than a single circuit was found to have a great advantage in ease of reproducing the measured potentials. The elements of one circuit served to check those of the second. Also, in effect, two runs were made under the same conditions at the same time, thus increasing efficiency.

A two-liter beaker served as the electrolysis cell. The catholyte consisted of 167 ml. of master solution [2.00 M. $Cu(NO_3)_2$] plus the addition agent. It was placed directly in the beaker. The anolyte was 25 ml. of master solution in a "Coors" porous clay battery cup of 5.0 cm. diameter. This cup contained the anode and rested in the beaker. It permitted the use of a copper anode when metal ions below copper in the electromotive series were added.

The cathodes, K_1 and K_2, were squares of smooth platinum foil, one centimeter on each side. The back and connecting lead of each was stopped-off with paraffin. A copper tube 2.5 cm. in diameter was the anode. The two reference electrodes were saturated calomel half-cells, C_1 and C_2. They were connected by saturated potassium chloride bridges to the common reservoir, E, of saturated potassium chloride.

The "capillary tips" were glass tubes drawn to capillary tips of one mm. outer diameter at one end. These ends were packed with asbestos fibers and the tubes were then partly filled with the master solution. The capillary tips were placed in firm contact with the faces of the cathodes, and, to complete the circuit to the calomel electrodes, bridges filled with a congealed saturated solution of potassium chloride with agar-agar led to the reservoir. The cells were immersed in a thermostatic bath which was kept at 25.0°C., controlled to within 0.1°C.

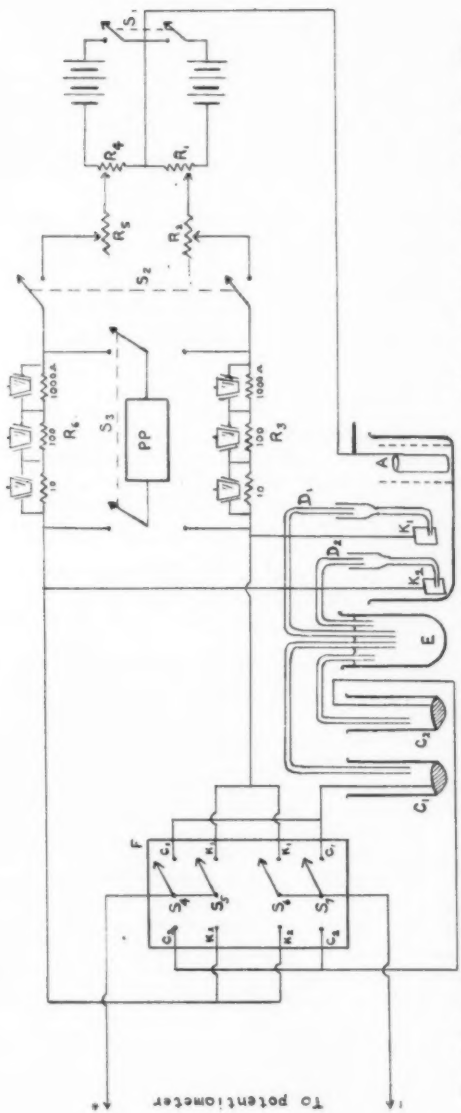

FIG. 1. The electrolysis and measuring circuit. K_1 and K_2, cathodes; C_1 and C_2, saturated calomel electrodes; E, reservoir of saturated KCl solution; A, anode; D_1 and D_2, gel bridges; PP, portable potentiometer; R_1, R_2, R_4, and R_5, sliding contact rheostats; R_3 and R_6, plug resistance boxes; S_1 and S_2, double pole, single throw switches; S_3, double pole, double throw switch; S_4, S_5, S_6, and S_7, single pole, double throw switches; F, switchboard (electrode leads labeled).

The potentials between any pair of electrodes (cathodes and calomel electrodes) could be measured to 0.0001 volt by the use of the panel of switches, F, and a Leeds and Northrup student potentiometer set-up.

Two 6-volt lead accumulators and four slide wire resistors provided adjustably variable sources of current. At some current densities, a very slight change in the current density would change the cathode potential by a large amount. A second potentiometer set-up across the standard resistors in series with each electrolysis circuit measured the current and enabled adjustments which kept the current at constant values, within ± 0.2 per cent.

The $Cu(NO_3)_2 \cdot 3H_2O$ was Merck's reagent grade. It was weighed on a torsion balance accurate to 0.05 g., dissolved in distilled water, and diluted to the mark in a volumetric flask. Several liters of this solution were prepared and the small amount of insoluble matter filtered out. Then the solution was stored in sealed glass bottles and used throughout the work as the master solution. The addition agents were chemically pure or reagent grade.

EXPERIMENTAL PROCEDURE

The electrolyte was measured into the cell. The platinum cathodes were cleaned anodically in dilute hydrochloric acid, then saturated with hydrogen by electrolyzing them cathodically in dilute sulfuric acid. They were rinsed with distilled water and immersed in the catholyte at once. After all connections were made, the catholyte was thoroughly stirred. However, there was no stirring during the runs.

It was decided to cover the range of current densities below 0.0320 ampere per square centimeter. This is a relatively broad range, starting above the current densities normally used in plating from a quiescent simple copper bath.

The run was started by throwing switches S_1 and S_2; this closed both plating circuits (see Fig. 1). The current in each circuit was rapidly adjusted to 0.0320 ampere.

Since the two circuits had the anode and electrolyte in common, it was necessary to keep the anode electrically symmetrical with respect to the cathodes. Thus, at the start of each run the anode was adjusted by means of its tiller handle and eccentric mounting so that there was no potential difference between the two cathodes (see Fig. 2). Careful attention kept the current constant during this operation. Eight minutes after the current was turned on, the potential was measured between C_1 and K_1 and between C_2 and K_2. Then the current was immediately adjusted to 0.0160 ampere in each circuit. Readings were taken and the current stepped down at eight minute intervals. This time interval was chosen because it was the shortest increment which would give reproducible results and the observed potentials were quite near the equilibrium values, within about one millivolt.

After each run was completed, the twin cathodes were withdrawn from the solution, rinsed with distilled water, and observed under a microscope. Then they were cleaned, saturated with hydrogen, and the run repeated at once using the same electrolyte. The second run on the same sample showed no significant difference in potentials from those of the first. This

was an indication that the possible small decrease in concentration of addition agent and any change in pH of the solution were negligible under the conditions encountered. Throughout the entire range of potentials of any run, the check run values differed, on the average by only 1 to 1½ millivolt.

The runs were made in descending order of current densities because (1) the platinum cathode was covered with copper and reached a stable potential sooner and (2) usually only one adjustment of the anode (see Fig. 2) at 0.0320 ampere kept K_1 and K_2 at equipotential throughout the run.

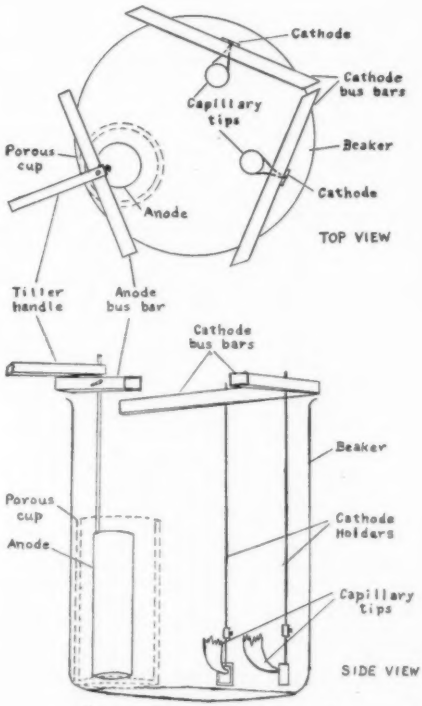

FIG. 2. The electrolysis cell

EXPERIMENTAL RESULTS AND DISCUSSION

Table I summarizes those addition agent concentrations which were used and the appearance of the deposit on removal from the cell at the completion of a run. For uniformity, all concentrations are expressed in milligrams of the simple cation per milliliter of catholyte. The surface of the electrodeposits was studied under a microscope with magnifications of 47 and 100 diameters.

Table II lists the averages of the potential measurements. In each case the recorded potential is that of cathode versus saturated calomel electrode.

The values of potential versus current density were plotted for each run and the resulting curves compared to the curve resulting from the plot of the control run values (no addition). Differences in potential at the same current density are attributed to the effects of the addition agent as all other conditions were held constant. On the basis of their effect on this

TABLE I. *Effects of addition agents*

Run	Addition agent	Grams added	Mg. of added metal per ml.	Appearance of deposit
1	H_3AsO_4	2.370	7.50	Uniform, compact plate of small grains. Dull pink.
2	H_3AsO_4	0.4740	1.50	Bright, adherent plate.
3	H_3AsO_4	0.0948	0.30	Bright, adherent plate. Finely striated.
4	$Ba(NO_3)_2$	0.7978	2.50	Smaller grained than control. Pink.
5	$Bi(NO_3)_3 \cdot 5H_2O$	0.0095[a]	0.024	Resembles control plate. Some blistering.
6	$Ca(NO_3)_2 \cdot 4H_2O$	2.460	2.50	Resembles control plate.
7	$Ce(NO_3)_3 \cdot 6H_2O$	0.625	12.07	Resembles control plate.
8	$Co(NO_3)_2 \cdot 6H_2O$	2.062	2.50	Smaller grained than control. Poor coverage.
9	Gelatin	0.100	0.67	Smooth, compact, dark plate. Some pitting.
10	HNO_3	0.497 (0.50 ml.)	0.062	Resembles control plate.
11	$Fe(NO_3)_3 \cdot 9H_2O$	3.0210	2.50	Resembles control plate.
12	$Fe(NO_3)_3 \cdot 9H_2O$	1.5105	1.25	Smaller grained, more compact plate than control.
13	$Pb(NO_3)_2$	2.2251	8.33	Resembles control plate.
14	$Pb(NO_3)_2$	0.0667	0.250	Poorly adherent, grain size slightly larger than control.
15	$Mn(NO_3)_2$	1.36	2.50	Grain size slightly larger than control. Poor coverage.
16	$Hg(NO_3)_2$	0.00539	0.020	Fine grained. Lower half of plate darker in color than upper half.
17	$Ni(NO_3)_2 \cdot 6H_2O$	20.685	25.0	Grain size slightly smaller than control.
18	$Ni(NO_3)_2 \cdot 6H_2O$	2.069	2.50	Same as for run 17.
19	$Ni(NO_3)_2 \cdot 6H_2O$	0.2069	0.250	Porous. Differs from control and runs 17 and 18.
20	$AgNO_3$	0.1320	0.500	Very poor gray, slimy plate.
21	$AgNO_3$	0.0330	0.125	Coarser grained than control. Purple-gray.
22	$AgNO_3$	0.0132	0.0500	More coppery than 21. Blackened readily in air.
23	$AgNO_3$	0.00132	0.0050	Finer grained than control.
24	TeO_2	0.00104	0.0050	Small compact grains but poor coverage. Appears smooth.
25	$Tl_2(CO_3)$	0.2394[a]	1.250	Resembles control plate.
26	$Th(NO_3)_4 \cdot 4H_2O$	5.9470	15.00	Resembles control plate.
27	$Th(NO_3)_4 \cdot 4H_2O$	0.5947	1.50	Resembles control plate.
28	$VO_2(NO_3)_2 \cdot 6H_2O$	1.761	5.00	Resembles control plate.

[a] ½ ml. of 70% HNO_3 added to dissolve addition agent.

curve in the region of moderate to high current densities, the addition agents may be divided into three classes:

Class 1 includes those addition agents which had no effect or very little effect on the polarization curve and on the deposit. Cobalt nitrate is outstanding in this class.

Class 2a is for those agents which displaced the curve but did not change

its slope. Barium nitrate, cerium nitrate, nickel nitrate, and silver nitrate are in this group.

Class 2b contains those addition agents which changed only the slope of the curve. Nitric acid and some concentrations of nickel nitrate and silver nitrate are in this group.

Class 3 is typified by those addition agents such as orthoarsenic acid and gelatin which change the shape of the curve, making it nearly logarithmic in nature. That is, the plot of the potentials versus the log of the current densities is almost a straight line.

TABLE II. *Current density*
Milliamperes per square centimeter

Run	32.0	16.0	8.00	4.00	2.00	1.00	0.500	0.250	0.100	0
control	0.1167	0.1209	0.1236	0.1252	0.1260	0.1265	0.1271	0.1288	0.1389	0.1415
1	.0900	.0993	.1098	.1170	.1204	.1227	.1236	.1250	.1274	.1338
2	.0801	.0909	.0995	.1080	.1126	.1177	.1207	.1235	.1260	.1317
3	.0784	.0871	.0957	.1032	.1068	.1098	.1146	.1198	.1234	.1325
4	.1112	.1178	.1226	.1247	.1256	.1261	.1266	.1285	.1377	.1400
5	.0901	.1078	.1187	.1242	.1266	.1279	.1286	.1289	.1297	.1370
6	.1128	.1198	.1237	.1256	.1268	.1272	.1281	.1294	.1420	.1446
7	.1104	.1163	.1192	.1224	.1235	.1241	.1248	.1257	.1236	.1360
8	.1167	.1214	.1237	.1252	.1261	.1266	.1270	.1282	.1378	.1410
9[a]	.0645	.0680	.0749	.0880	.1013	.1087	.1130	.1156	.1184	.1327
10	.0915	.1077	.1178	.1232	.1259	.1273	.1281	.1285	.1293	.1366
11	.0996	.1128	.1209	.1242	.1265	.1277	.1375	.1404	.1412	.1414
12	.1080	.1178	.1237	.1261	.1275	.1283	.1289	.1373	.1403	.1407
13	.1093	.1166	.1205	.1228	.1242	.1248	.1253	.1259	.1309	.1370
14	.1113	.1183	.1219	.1239	.1251	.1258	.1262	.1271	.1394	.1420
15	.1127	.1193	.1231	.1251	.1264	.1271	.1275	.1287	.1374	.1408
16	.1110	.1161	.1186	.1199	.1203	.1205	.1208	.1246	.1322	.1329
17	.1151	.1220	.1263	.1284	.1296	.1305	.1309	.1315	.1347	.1397
18	.1100	.1167	.1208	.1230	.1245	.1252	.1262	.1271	.1326	.1371
19	.1132	.1185	.1214	.1231	.1242	.1249	.1255	.1266	.1343	.1385
20[b]	.1085	.1127	.1145	.1173	.1203	.1229	.....	.....	.....	.....
21	.0032	.1053	.1130	.1173	.1201	.1227	.1262	.1342	.1372	.1378
22	.0977	.1092	.1155	.1190	.1210	.1232	.1262	.1295	.1348	.1354
23	.1116	.1184	.1207	.1225	.1234	.1241	.1249	.1258	.1367	.1406
24	.1179	.1223	.1230	.1228	.1222	.1244	.1247	.1292	.1383	.1410
25	.0896	.1057	.1163	.1211	.1235	.1248	.1256	.1261	.1269	.1322
26[c]	.1049	.1150	.1212	.1246	.1266	.1288	.1290	.1293	.1298	.....
27	.1115	.1180	.1218	.1250	.1262	.1271	.1277	.1282	.1289	.1362
28	.1151	.1200	.1238	.1248	.1259	.1266	.1272	.1279	.1292	.1355

[a] Not checked closely
[b] No reproducible readings at lowest current densities
[c] Readings taken when equilibrium was reached—in all cases at 8 minutes or less.

Fig. 3 through 8 illustrate classes 2a, 2b, and 3. The potential differences are less pronounced at the lowest current densities used.

When several concentrations of the same addition agent were used, in some cases a maximum was noted in the potentials recorded at a given current density. A semiquantitative study with nitric and phosphoric acids as addition agents showed minima. Addition of nickel nitrate gave both a maximum and a minimum. This is shown in Fig. 9. The units for plotting are arbitrary, but the change in potential may be as large as

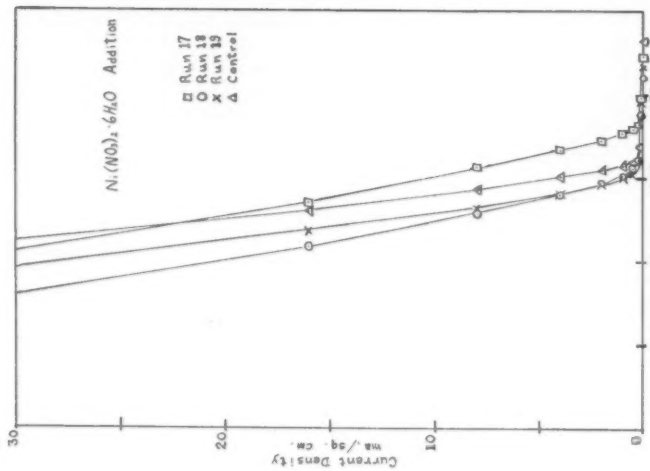
$Ni(NO_3)_2 \cdot 6H_2O$ Addition
Run 17
Run 18
Run 19
Control
Current Density
ma./sq. cm.
30
20
10
0
.1050
.1150
.1250
.1350
E.M.F. (Cathode vs. saturated calomel cell)
volts

FIG. 4

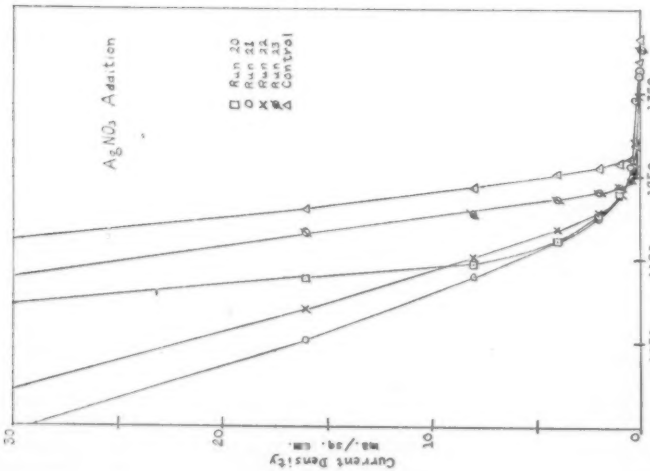
$AgNO_3$ Addition
Run 20
Run 21
Run 22
Run 23
Control
Current Density
ma./sq. cm.
30
20
10
0
.1050
.1150
.1250
.1350
E.M.F. (Cathode vs. saturated calomel cell)
volts

FIG. 3

FIG. 3

FIG. 4

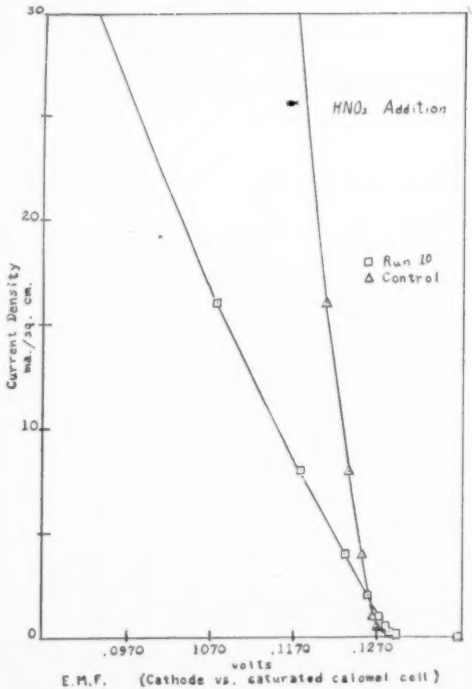

FIG. 5

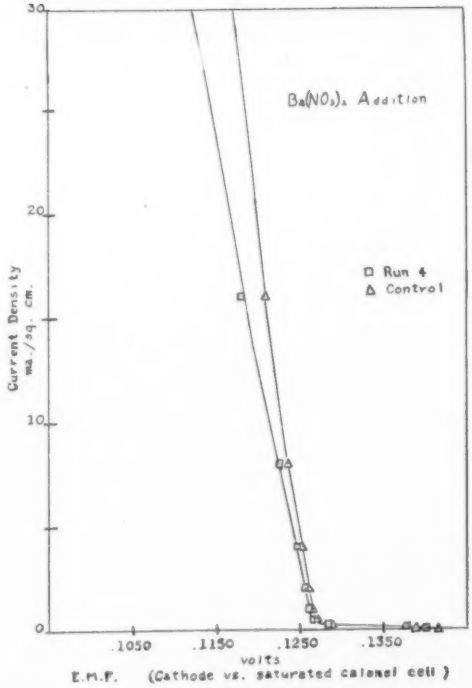

FIG. 6

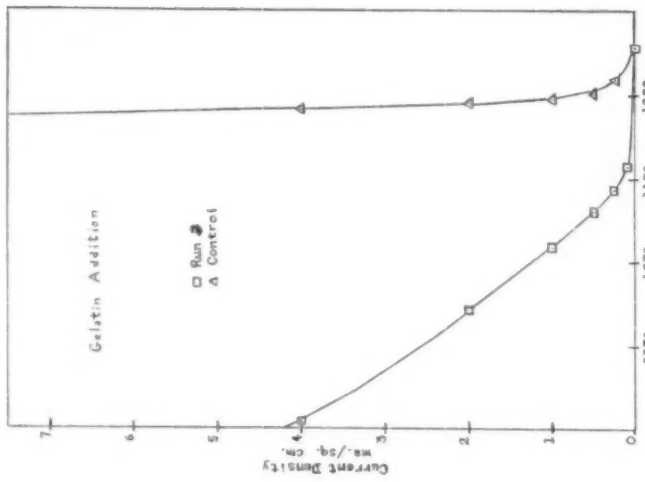
Gelatin Addition
□ Run 3
△ Control
Current Density
ma./sq. cm.
E.M.F. (Cathode vs. saturated calomel cell)
volts

FIG. 8

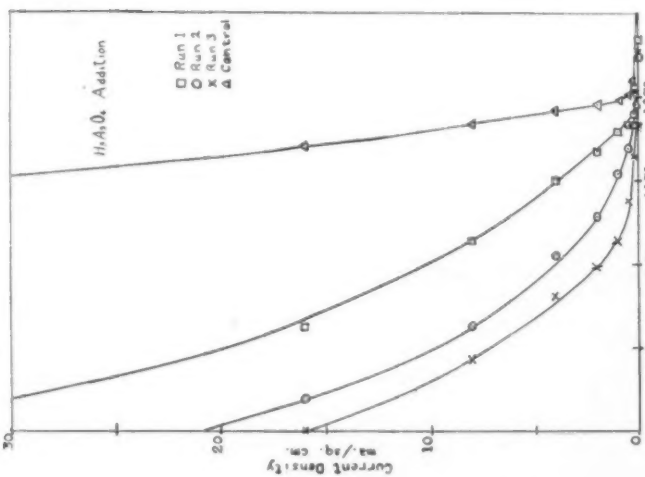
H_3AsO_3 Addition
□ Run 1
○ Run 2
× Run 3
△ Control
Current Density
ma./sq. cm.
E.M.F. (Cathode vs. saturated calomel cell)
volts

FIG. 7

several millivolts. The curves are plotted at constant current density. E_c is the potential for the control (no addition) at this current density.

Results similar to these have been reported (3) for hydrogen overvoltage on platinum, silver, and copper electrodes when variable amounts of gelatin were added to $2NH_2SO_4$. These workers found that the point of maximum potential does not depend on the electrode metal. Absorption compounds between ions of acid and the colloid were offered as a possible explanation.

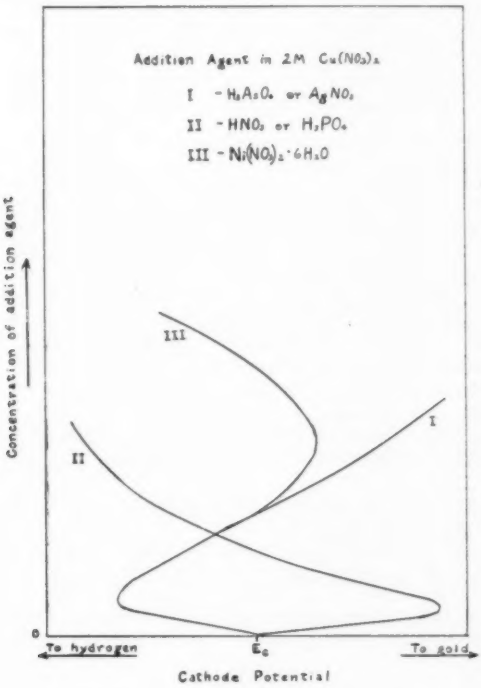

FIG. 9

Since the shape of the curve is changed by the addition of a Class 3 addition agent, a different step in the electrodeposition process is the slow one. More data will be needed to give a specific explanation of the changes in potential.

The last column in Table I gives the results of the microscopic study of the faces of the cathodes after the completion of a run. There is no apparent relationship between polarization and grain size on the basis of this work.

It is realized that the deposits were very thin and were deposited at varying current densities. On another basis metal and at a constant current density, a thicker deposit might not show the same differences with respect

to the control deposit. However, thicker deposits (made at 0.0160 ampere per square centimeter for two hours on copper foil) from test solutions identical to those used in the runs showed the same general changes as the thin deposits on platinum.

Meyer and Phillips (1) found that silver ions decreased cathodic polarization the most (of the cations studied) and had the greatest roughening effect on the deposit from a cuprocyanide bath. Lead ions increased polarization the most and had the greatest brightening effect. However, the results published in this work on the simple cupric nitrate bath shows silver ions to be strongly polarizing at low concentrations and that they made the surface of the deposit more coarse. In this bath, lead had little effect on either the polarization or the character of the deposit. This emphasizes the point that depolarizers, brighteners, etc. are quite specific, that is, addition agents are beneficial only to certain baths under definite conditions.

SUMMARY

The conclusions drawn from this research are summarized as follows:

1. The twin cathode apparatus is believed to have definite advantages over the usual single cathode set-up. The elements of one circuit served as a check on the other, it was faster to use, and the ease of obtaining reproducible results was increased.

Taft's hypothesis seems to give a plausible explanation for the form of the potential versus current density curve of the control run.

3. Ionic addition agents are shown to have a small effect on the cathode potential in comparison to that of a colloidal addition agent.

4. The most desirable deposits from the cupric nitrate bath on copper as the basis metal were obtained with additions of orthoarsenic acid and of a solution of thallous carbonate with nitric acid. Orthoarsenic acid acted as a brightener and the solution of thallous carbonate with nitric acid gave a dense, fine grained plate.

5. No definite relationship could be found between cathode polarization and the grain size of the deposit.

6. Maxima and minima of polarization were found when varying concentrations of some of the same addition agents were used.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

REFERENCES

1. W. R. Meyer and A. Phillips, *Trans. Electrochem. Soc.*, **73**, 377 (1938).
2. R. Taft, *Trans. Electrochem. Soc.*, **63**, 75 (1933).
3. N. Igarischew and S. Birkmann, *Z. Electrochem.*, **28**, 47 (1922).

THE OXYGEN EFFICIENCY IN ANODIC OXIDATION OF ALUMINUM[1]

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ABSTRACT

This paper describes experiments that lead to the abandonment of the view that anodic coatings on aluminum "grow inward" because of slow chemical solubility of the oxide. It introduces the idea of "oxygen efficiency," which represents the fraction of electricity passed through an anodizing cell that is responsible for formation of aluminum oxide, the remainder causing either generation of free oxygen or anodic dissolution of the metal. This leads to simple algebraic expressions permitting correlation of current density, temperature of electrolyte, and concentration with this efficiency. Graphs of measurements of this nature indicate a close parallelism with an abrasion test used for evaluating quality of anodic coating. Subsequent adjustment of the theory to take into consideration chemical solubility of oxide leads to mathematical expressions showing that the oxide coating grows to a maximum thickness, in agreement with experimental results in an important paper by Mason and Slunder. An expression for oxide loss by chemical solution is also derived which is supported by measurements in the same paper.

ASSUMPTIONS AND DEFINITIONS

In order to facilitate enunciation of statements and to avoid misunderstandings, it will be desirable to specify the meanings of certain terms and to clarify some concepts.

1. Aluminum, and those of its alloys with which this investigation is concerned, is only sparingly soluble chemically in sulfuric acid solutions of the concentrations employed. Table I shows typical results on solubility.

As most anodizing experiments recorded herein were carried out with the specimens immersed in solutions less than 25 minutes, it is not necessary to take into consideration chemical solution of the metal after more prolonged attack, although the theory given below is capable of extension to include this item.

2. As a first approximation, the chemical solubility of aluminum oxide formed during the anodic oxidation process is left out of consideration, although at the higher temperatures considered here the solution rate is appreciable. Subsequently, the theory is extended to take care of this item, and it will be seen that the fundamental ideas do not require drastic modification, the correction being essentially in the form of an additive term.

3. *Anodic solubility* of *aluminum oxide* is not conceded because, in order that a substance shall be attacked anodically, it must be a conductor.[2]

The fact that chemical solubility of the oxide is not considered at first,

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[1] Manuscript received July 16, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

[2] See reference 7, page 1603, left column, where this possibility is *not* ruled out.

in order to arrive at the new theory, makes it necessary to abandon the view expressed in the literature[3] that the porosity of the anodic coating is caused by the slow solubility of the oxide and that film growth would cease if the film were insoluble. In fact, it will be seen that the converse view would be more appropriate: the less porous the film, the less the chemical dissolution. Moreover, the porosity is largely responsible for the rapid dissolution of the oxide at elevated temperatures. The essential reason for porosity will become apparent on the basis of the revised theory given below. The current theory is untenable, since on it the growth of the film is dependent upon the slow solution of the coating. This is said to give rise to pores through which further growth can take place. But chemical solubility at a given temperature and concentration is a constant, while on the other hand it is known[4] that increasing the current density will markedly increase the rate of formation of the oxide film. This will also become apparent from the experimental evidence adduced below.

4. The oxide formed during anodic coating occupies more space than the metal from which it was formed (**2, 8**). This causes gradual loosening

TABLE I. *Chemical solubility of aluminum, alloy 52 S-O, in 17.5 per cent sulfuric acid. Immersion time 25 min.*

Temperature		Loss from 12 sq. in. (77.5 sq. cm.) area, grams	Number of specimens averaged
°F.	°C.		
80	26.7	.0007	5
90	32.2	.0010	7
100	37.8	.0017	7
110	43.3	.0022	5
120	48.9	.0040	5
160	71.1	.0097	11

and coarsening of the oxide particles which are eventually dislodged, assuming a chalky state on the upper layer of oxide. This can be rubbed off by wiping, and, when passing the finger over such a surface, a white residue is found on the finger. It follows that this so-called chalking of the surface of the oxide is caused chiefly by the rapid formation of expanding oxide in the metal layers underneath, and only to a limited degree by chemical attack. This point is supported experimentally by the observation that, while chalking can be produced by subjecting the coating to chemical attack by the acid alone, this necessitates immersion for protracted periods at ordinary temperatures, or elevation of the temperature.

5. The unhydrated oxide, Al_2O_3, is formed in sulfuric acid solutions of the kind employed here,[5] and although water might be absorbed in the porous film, great care was taken to insure complete removal of all uncombined water by abundant use of a desiccator. Many blank runs were made, the specimen being first dried in a desiccator, then weighed, and then

[3] See, for example, reference 1, page 858, and reference 8, page 135.

[4] See reference 5, page 125 (for graphs), and page 128.

[5] This is generally admitted in the literature. See, e.g., reference 1, pp. 859 and 860. On this last page, the description of the sealing process implies the formation of the unhydrated oxide. See also reference 2, page 160; 8, p. 136; and 9 passim.

subjected to prolonged high vacuum treatment at pressures less than 0.001 mm. Hg. Subsequent weighing rarely revealed more than 0.05 per cent error.

PRELIMINARY EXPERIMENTS

If a piece of aluminum, 2 in. by 3 in. by about 0.030 in. (5.08 x 7.62 x 0.076 cm.) thick, is carefully weighed and then subjected to anodic oxidation in a conventional sulfuric acid solution of 15 per cent concentration or so, at 12 amp./sq.ft. (1.29 amp./sq.dm.) for 10 minutes, the weight increase would be 0.04973 gram if all the current generated oxygen, and all the oxygen formed anhydrous aluminum oxide. This increase is a sufficiently large fraction of the total weight of the specimen, so doubt will hardly be thrown upon results through errors in weighing. If this weight increase had actually occurred, 100 per cent anodizing efficiency would be ascribed to the cell in the ordinary parlance of electrometallurgists.

Actually the weight increases found in such experiments are far below expectations.[6] Table II gives typical results for a series of experiments carried out at 70°F. (21.1°C.) (at which temperature production work is

TABLE II

Current density		Weight increase grams
amp./sq. ft.	amp./sq. dm.	
12	1.29	0.0225
18	1.94	0.0252
24	2.58	0.0272
36	3.87	0.0293
48	5.16	0.0298

frequently carried out), all specimens being treated for 120 amp.min./sq.ft. (12.9 amp.min./sq.dm.).

It is, of course, conceivable that free oxygen is generated and escapes into the atmosphere. To determine whether this was true, a gas-collecting tube was arranged so that the entire specimen was surrounded by its lower portion which tapered upward into a narrow-bore tube graduated into tenths of a cubic centimeter, generally after the style of a eudiometer tube. The whole was filled with electrolyte, so that any gas forming at the electrode could be collected by displacement. It was found that the oxygen so collected was entirely insufficient to account for more than a small fraction of one per cent of the total current passed. This result was responsible for the development of the theory to be described in the next paragraph.

It may be mentioned that, for the purposes of the experiments, all specimens were held in Lucite (methyl-methacrylate plastic) holders in which were buried tungsten wires, a small portion of which was exposed for making

[6] References 4, 6, 8, and 9 all observe this, but the explanation in 4, Scott Anderson, only, is similar to that herein, although there are no assumptions about micro-occurrences, this being unnecessary for the present theoretical development. Furthermore, Scott's quantitative statements do not agree with measurements reported herein.

contact to one edge of the aluminum part. Tungsten rapidly passivates in sulfuric acid when subjected to anodic attack, and, in the experiments reported here, for a second or so after closing the circuit, oxygen collected on the exposed tip. This was seen to escape into the collecting tube above the electrode. Occasionally, a small bubble would stick to the wire. The gas coming from the wire would trickle upward quite rapidly and cease forming almost instantly. The total amount collected was always less than 0.5 cc. (NTP) out of a possible 185 cc. or so of oxygen. It will be seen from the theoretical formulae developed that this is too small a percentage to make any appreciable difference in the results of computation. During the entire period of anodizing, small quantities of oxygen would form into bubbles and rise slowly to the top of the collecting tube. They seemed to form either on sharp protrusions of the specimen or on visible impurities in the metal; always they had the appearance of minute bubbles that slowly grew until buoyant enough to float upward. In no case was a total of more than a half per cent or so of the total current involved, and, in one series of experiments involving a total current that could be responsible for generation of about 225 cc. oxygen (NTP), only 0.5 cc. was actually liberated and collected.

THEORETICAL CONSIDERATIONS

The preceding experiments made it suggestive to assume that *anodic* solution of aluminum occurs during the oxidation process, so that the following processes take place simultaneously:

1) Oxygen is generated and escapes into the atmosphere;

2) Oxygen is generated and rapidly combines with aluminum of the electrode to form Al_2O_3;

3) Aluminum is dissolved anodically, forming aluminum sulfate.

These three processes account for all the current consumed and no assumptions of any other kind are required for the development of the theory which follows. They are subject to verification by measurement, the only errors introduced being due to solubility of both metal and oxide which are at first neglected. Only in one previous publication (6) has the suggestion of anodic solution of aluminum been made explicitly. In that paper,the author devised an ingenious micro-mechanism to explain occurrences at the anode. It is not necessary for the present purposes either to accept or to reject that theory since only the macro-observations indicated above are used in obtaining the results that follow. It is hoped, however, to revert to a discussion of the quantitative conclusions drawn from Scott Anderson's theory at some future opportunity.

In another publication,[7] the suggestion is made, but is not finally adapted as an assumption, that anodic solution *might* occur. The text there seems to imply acceptance of a previous theory[8] that all current passed through the cell is used for making oxygen and all this is converted to aluminum oxide (In sulfuric acid; with other electrolytes, suitable exceptions are of course made) which in turn is partly dissolved. This seems an unnecessarily complicated mechanism that is subject to criticism on other grounds as well. Furthermore, it contradicts Scott Anderson's theory.

[7] See reference 7, page 1605, top left column.

[8] See abstract in reference 8, page 139, and elsewhere in that paper.

Now let q_o denote the fraction of electricity passed through the cell that liberates oxygen for the formation of oxide, and q_a the fraction that dissolves aluminum anodically. Then, since oxygen discharge into the atmosphere is neglected, we have,

$$q_o + q_a = 1. \tag{1}$$

Let $e_o = 0.004974$ g./amp.min. denote the electrochemical equivalent of oxygen, and $e_a = 0.005707$ g./amp.min. the corresponding quantity for aluminum anodically dissolved.

Then, in t minutes the oxygen generated by A amperes is $q_o e_o At$ grams, and the aluminum dissolved is $q_a e_a At$ grams. Let w grams be the weight increase (which may be negative or positive) of the specimen. Then,

$$q_o e_o At - q_a e_a At = w. \tag{2}$$

From (1) and (2) follow, inserting the numerical values,

$$q_o = 0.53440 + 93.624 \frac{w}{At} \tag{3}$$

$$q_a = 0.46568 + 93.624 \frac{w}{At}. \tag{4}$$

The quantity q_o multiplied by 100 is defined as the oxygen efficiency of the process at the current density, temperature, concentration, and other operating conditions of the cell. Similarly, q_a multiplied by 100 is the aluminum anode efficiency.[9]

From equation (3), it may be concluded that the oxygen efficiency is at least 53.4 per cent as long as a positive weight increase is found from measurement, but a weight decrease by no means signifies absence of oxide coating. Complete absence of coating is obtained when the oxygen efficiency is zero, that is, when the ratio of weight loss to electricity consumed is 0.00570.

The formulae also make it possible to calculate the amount of oxide that may be applied so that no alteration of dimensions of the specimen takes place; this, of course, presumes a knowledge of the density of the oxide and previous measurement of the oxygen efficiency of the cell. Further, the actual oxide thickness from measurement of the specimen thickness before and after processing is ascertainable.

EXPERIMENTAL RESULTS

The operating conditions are generally given on the corresponding graphs. Electricity consumption in ampere minutes was carefully measured by time and ammeter readings, and checked by having a copper coulometer in series with the cell.

[9] See reference 5, page 121, where Fig. 56 shows gain in weight of aluminum in relation to electricity consumed. In the text, no adequate explanation is offered for the low value exhibited by the measured curve as compared with the theoretical. The 5 per cent or so oxygen said there to escape into the atmosphere from the oxalic acid electrolyte, plus that consumed in oxidizing this acid to carbon dioxide, is easily shown to be insufficient to bring the two curves to coincidence. It may be mentioned here that the oxygen efficiency defined above may be correlated without great difficulty to the idea of "coating ratio" evolved by Edwards and Keller in reference 8.

Numerous and elaborate tests were made in the endeavor to correlate the oxygen efficiency measurements with some form of numerical quality evaluation of the anodic coating. There are available various methods of measuring thickness of coating, e.g., by microscope on a section of anodized aluminum; by the beautiful but apparently little tried or developed method of stripping off the coating described by Wernick;[10] by the filmeter method (3); by micrometer thickness measurement of the specimen before and after processing (and subsequent calculation in accordance with equation (3) above). There is the important method given by Edwards (4)[11] of stripping off the coating with a phosphoric acid-chromic acid mixture, weight difference before and after giving a measure of the coating thickness. There are methods of measuring quality by means of testing dielectric strength of the oxide,[12] and finally the methods of measuring abrasion resistance.[13]

It should be pointed out that the oxide stripping method gives results that can clearly be made to agree with the results given below, and with the results of abrasion resistance if equation (3) is taken into consideration. The difference between this and the present method is that in the oxide stripping method one measurement is made after anodizing and one after stripping, while in the one reported herein one measurement is made before anodizing and one after; two measurements are obviously necessary to fulfil the requirements of the equations given.

The easiest, practical measurements are undoubtedly the filmeter and dielectric strength measurements. With neither has correlation been obtained with the results of measurements reported here and on the basis of equation (3). In Fig. 5a and 5b are shown typical results, and it should be emphasized that a very large number of similar measurements were made throughout the entire range of experiments performed. Parallel with all weight differences ascertained were both dielectric strength and filmeter measurements. The source of error here is probably of twofold origin. On the one hand, the coating is very thin, making any kind of thickness measurements extremely difficult. On the other, with either the present theory of anodic dissolution of aluminum, or that of chemical solution of metal and oxide, there is no guarantee that all the aluminum in the coating is converted to oxide, especially for very thin coatings. It is quite conceivable (unless new evidence proves the contrary) that an aluminum particle, an isolated island or a peninsula, so to speak, may be completely or almost completely surrounded by oxide without having itself been subject to anodic attack. Such a particle would give rise to low apparent thickness readings in the case of the filmeter, and to premature breakdown of the film in the dielectric strength tests.[14]

Excellent agreement was obtained by subjecting the parts to an abrasion test[15] which consists of blowing a stream of carefully graded abrasive, such as alundum, against the specimen under controlled conditions, so as to imitate sandblasting, and observing when the coating is penetrated. The

[10] Reference 2, page 165.
[11] See also *ASTM Standards*, Part 1, page 1164, 1942.
[12] e.g., *ASTM Standards*, Part 1, page 1161, 1942.
[13] Reference 5, page 140, and especially reference 9.
[14] Reference 9, page 528, indicates that rather wide variation in dielectric strength readings may be expected.
[15] This type of test is described in reference 9.

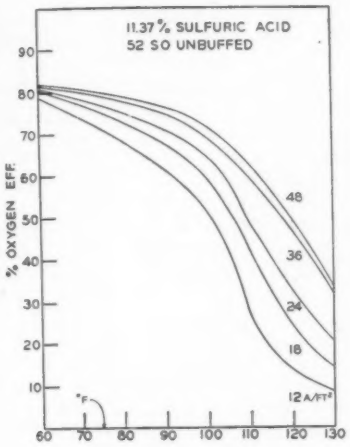

FIG. 1a

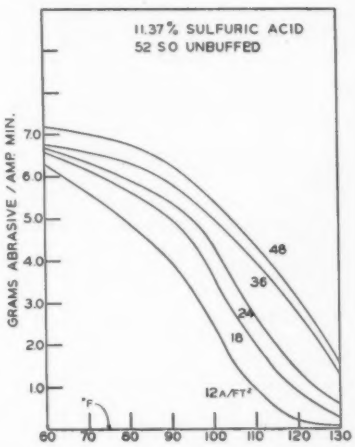

FIG. 1b

FIG. 1a and 1b. Comparison of oxygen efficiency and abrasion resistance plotted against temperature at various current densities. Aluminum alloy 52 S-O, unbuffed surface.

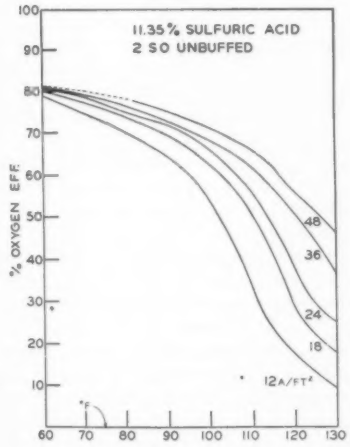

FIG. 2a

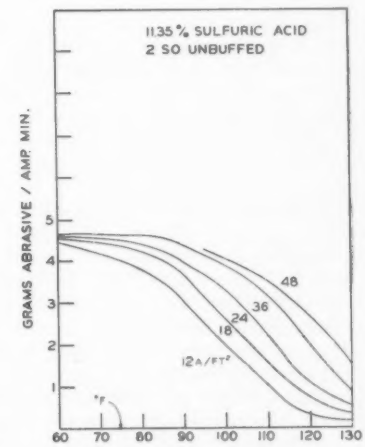

FIG. 2b

FIG. 2a and 2b. Comparison of oxygen efficiency and abrasion resistance plotted against temperature at various current densities. Aluminum alloy 2 S-O, unbuffed surface. Note that abrasion resistance of coating on this alloy is lower than for 52 S-O, but this need not be so under all conditions. See e.g., reference 9.

grit is blown over a well-defined area which, at its center, is subject to especial impingement. At this spot, which is about one-eighth inch in

diameter, a dark color appears when the oxide is penetrated. The weight of grit required for penetration serves as a measure for abrasion resistance. This is plotted against the same variables as in oxygen efficiency graphs.

At temperatures over 80°F. (26.7°C.), scarcely any irregularities occur, all values being found to lie on smooth curves of the type shown in Fig. 1a, 1b; 2a, 2b. At very low temperatures, especially below 70°F. (21.1°C.), and at high current densities, a curious effect was found with all alloys that were employed. The weight increase was much less than anticipated, the oxygen efficiency was considerably reduced, and the abrasion resistance was reduced to negligible values. The occurrence, while not universal, may be so frequent that it may easily be misinterpreted as a normal phenomenon. Close examination reveals that the specimen is only slightly anodized except near some corner or edge, where a bright oxide forms. This is very much harder than the usual variety and, apparently, much less porous. It penetrates deeply into the basis metal, which, upon prolonged exposure to the effect, turns entirely into this bright oxide. Production of a complete specimen covered with this oxide all over has not been possible heretofore. Upon subjecting the area so attacked to abrasion tests, extraordinarily high values are found, and it is almost impossible to buff off the spot. Reproduction of the phenomenon in such small areas as generally occur, i.e., about one-half inch in diameter, adjacent to an edge or corner, is not difficult. The occurrence can be observed during the anodizing process, since considerable oxygen is liberated at these spots, and there is evidence that current concentrates there, thus apparently eliminating the usual "current-uniformizing effect" of the anodic coating as it forms in the normal manner.

Fig. 1a shows the oxygen efficiency as obtained by means of equation (3) from a number of specimens of 52 S-O alloy, plotted against temperature, the current density being used as parameter. Fig. 1b shows corresponding results from the same specimens where abrasion resistance is taken as the dependent variable. All specimens were subjected to 240 amp.min./sq.ft. (25.8 amp.min./sq.dm.) but equally good agreement was found when 120 amp.min./sq.ft. (12.9 amp.min./sq.dm.) or other values were employed, indicating the sensitivity of the measurement. The abrasion resistance is given in grams of abrasive required for penetrating the coating, divided by the number of ampere minutes used. Clearly, this is simply a convenient unit which does not artificially displace results. An obvious alternate would have been grams abrasive per ampere minute per square foot, but this would only have changed the scale.

The resemblance between graphs of Fig. 1a and Fig. 1b is so close that evidently both quantity of oxide and hardness are paralleled by the oxygen efficiency. When the 52SO aluminum specimens are buffed and data are plotted, the curves for all practical purposes are identical to those shown in Fig. 1a and 1b. The irregularities, which are found in the abrasion resistance measurements, would be expected, since this is a fairly rough measurement, and the size of dark spot where initial penetration occurs must be estimated by the operator. Differences in aluminum surface sometimes cause a different appearance of the spot, but generally speaking this applies to all specimen of one run. The error introduced, therefore, applies to complete sets of curves rather than to individual points on them.

Fig. 2a and 2b show the results obtained with alloy 2 S-O, i.e., commercially pure aluminum. These agree closely in character with the previous ones, and it was not thought necessary to multiply graphs further in this record.

Fig. 2b compared with Fig. 1b shows that coatings on high purity aluminum *may* very well have low abrasion resistance—contrary to an observation made previously.[16]

In Fig. 3, the results of Fig. 1a have been replotted in terms of current density against oxygen efficiency, the temperature now being regarded as parameter. It is seen that increased current density generally improves efficiency as does lowered temperature. This is to be expected. However, increase of current density does not improve the efficiency in the same proportion at lower temperatures as it does at higher temperatures, even without taking into consideration the special effect mentioned above, which is responsible for the sharp drop in efficiency indicated by the dotted lines.

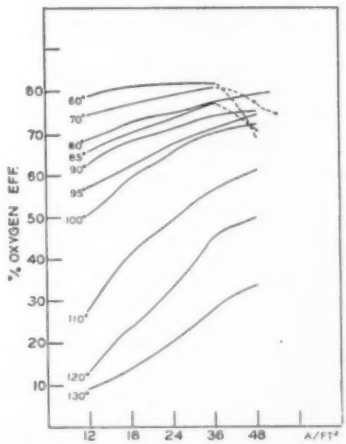

FIG. 3. Results of Fig. 1a replotted using temperature as parameter

A number of sets of specimens were processed at very low temperatures. In Fig. 4 are shown the results for 21° and 50°F. (−6.1° and 10.0°C.). At the lower temperature, the solution began to freeze, so that still lower temperatures could not be investigated. The highest oxygen efficiency recorded in all experiments was at a current density of 12 amp./sq.ft. (1.29 amp./dm.sq.) 21°F. (−6.1°C.) for 10 minutes. The efficiency was 91.14 per cent. The abrasion resistance was excellent but was not the maximum found.

In Fig. 5a and 5b are shown results that were typical of measurement with filmeter and dielectric-strength meter (9). The readings given are averages of eight to ten measurements, the total spread of which did not exceed 10 per cent in any single run. The results correspond neither to

[16] Reference 9, page 140.

each other nor to abrasion resistance measurements and oxygen efficiencies computed, probably for the reasons already outlined above in connection with the first comments on Fig. 5a and 5b.

EFFECTS OF OXIDE SOLUBILITY

Two experimental methods were tried for determining the effects of oxide solubility. The first was to anodize and dry the specimen; weigh it; subject it to acid attack alone, under the same conditions used for anodizing except no current; and, finally, dry and reweigh once more. The loss observed after the acid attack would serve as a measure of solubility, and it was thought reasonable that this amount should be added back to the specimen weight after anodizing, on the assumption that during the latter period substantially the same amount of oxide dissolved. This procedure,

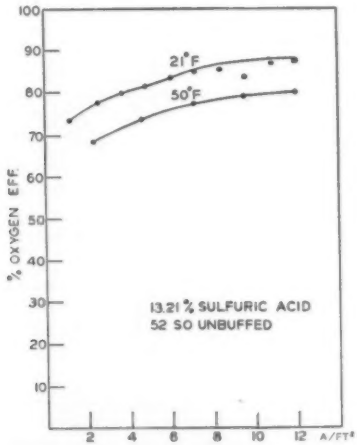

FIG. 4. Results of processing at extremely low temperatures. Highest oxygen efficiency recorded was over 91 per cent.

however, yields erratic results and is open to various objections. At the beginning of the anodizing process, chemical attack by the acid on the coating is *not* a linear function of time, because there is only a small amount of oxide present. Irregular wetting by the solution, once the specimen has been dried, retards initial attack after reimmersion in the acid. There are also other factors, such as penetrating speed of the acid through the porous oxide, etc., that are difficult to measure and consider. All or some of these factors may be responsible for the erratic results which caused this method to be abandoned.

The second method is to anodize two specimens simultaneously under identical conditions and in the same solution; leave one in the solution for chemical attack alone for a period equal to the anodizing period; plot the results for the first specimen as before, while the second one is dried and

reweighed after the additional acid attack; and, then, the result treated as though no acid attack had taken place. Fig. 7a shows the result with acid attack, and Fig. 7b shows the result with the specimen not subjected to acid attack after anodizing. It is clear that the *character* of the curves is unchanged through ignoring acid attack. It need hardly be emphasized that the oxygen efficiency in Fig. 7a is too low, and a formal procedure for inferring quantitative correction would be difficult to develop from these graphs alone, but it is hoped that this may be taken up at a later opportunity.

The general considerations in this paragraph suggest, however, a quantitative mechanism for oxide solubility. At the beginning of the anodizing process there is very little oxide present, and it is reasonable to suppose that

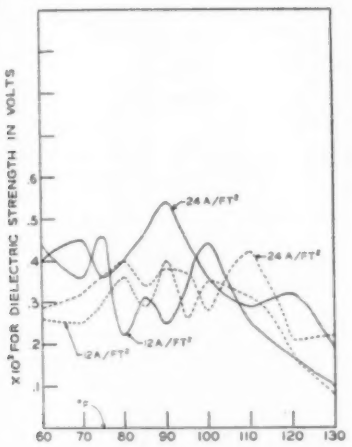

FIG. 5a

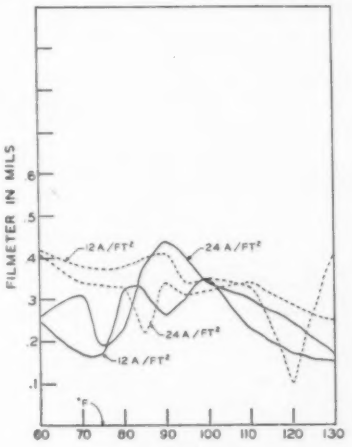

FIG. 5b

FIG. 5a and 5b. Dielectric and filmeter tests on samples for which oxygen efficiencies and abrasion resistance was plotted in Fig. 2a, 2b, showing erratic results obtained with these as compared with abrasion resistance tests. (---unbuffed corresponds to Fig. 2a and 2b.)

chemical attack is then proportional to the amount of oxide present. This can be expressed mathematically as follows: Let $Q(t)$ be the quantity of oxide present t minutes after commencement of anodizing, and let $Q(O) = O$. The rate of change of oxide is of course dQ/dt which is equal to the oxide gained by electrolytic formation minus that dissolved, in unit time. If A represents amperes flowing through the specimen, the rate of gain is $Ae_o q_o$, and the loss is proportional to the quantity of oxide present, or sQ, where s is a solubility constant (i.e., independent of time) and the remaining notation is the same as previously employed.

Hence,

$$\frac{dQ}{dt} = Ae_o q_o - sQ.$$

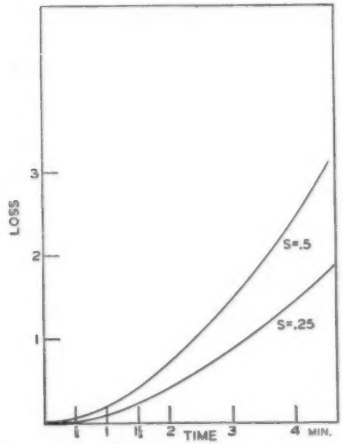

FIG. 6. Graph of function (6) for loss by chemical attack on oxide when simultaneously subject to anodizing process. Loss units arbitrary. Compare this graph with dotted graph in Mason and Slunder's Fig. 5, reference 7.

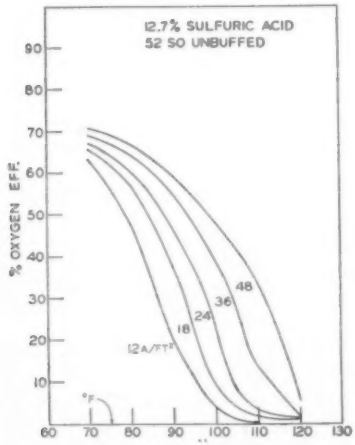

FIG. 7a

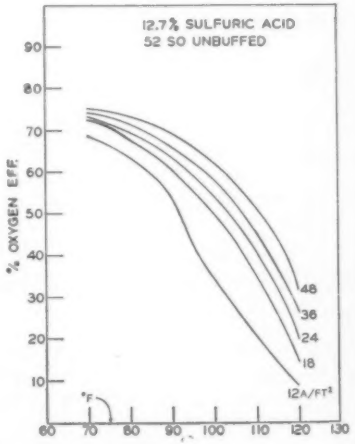

FIG. 7b

FIG. 7a. Oxygen efficiencies on anodized samples subjected to additional chemical attack for period equal to anodizing.

FIG. 7b. Identical specimen as 7a, but not subjected to additional chemical attack after anodizing.

This differential equation has the solution

$$Q(t) = \frac{Ae_o q_o}{s}(1 - e^{-st}). \qquad (5)$$

It is probable that s is Arrhenius' function of absolute temperature, e.g., C/T where T is the absolute temperature and C is independent of temperature and time, but this has not been investigated.

The loss at time t is then given by the expression

$$L(t) = Ae_o q_o \left\{ t - \frac{1}{s}(1 - e^{-st}) \right\}. \quad (6)$$

Equations (5) and (6) attain some significance in the light of measurements recently published in an important paper by Mason and Slunder (7). The curves in Fig. 4, page 1606, of that paper give excellent support for equation (5), and in fact indicate that the porous nature of the oxide maintains the condition that the rate of change of oxide is proportional to the amount of oxide present at all times. Equation (5) further states that the coating quantity asymptotically approaches the maximum $Ae_o q_o/s$, and this is exactly the behavior indicated in Mason and Slunder's Fig. 4.

The dotted curve in Fig. 5 of Mason and Slunder's paper reveals the shape of function (6) above, which is depicted with arbitrary units on the loss scale in Fig. 6. From Mason and Slunder's Fig. 5, it would not be difficult to derive the value of the solubility constant s. One would ordinarily expect the loss curve caused by chemical solution to become linear, because on the one hand, the coating becomes constantly thicker, and on the other hand, the acid in the pores would be expected to become saturated with solution, so that the rate of attack rapidly attains a constant value. Hence, the expectation would be for the coating surface to present essentially a plane for chemical attack, for which, obviously, a linear time law subsists. This is not the case, according to function (6) and Mason and Slunder's dotted curve in their Fig. 5.

A conclusion may be drawn from these observations: *The surface area of the coating and its pores is proportional to the volume of oxide present.*

The remaining graphs in Fig. 5 of Mason and Slunder's paper (the solid lines) show an unexpected phenomenon. The curves become *steeper* as time proceeds, indicating *increasing* rate of solution.[17] The same observation was made by the present author in measurements not included in this paper; but the opportunity may be taken to make the following additional statements. At first, when a coated article is subjected to chemical attack alone, the rate of solution *increases*, probably because wetting and penetrating resistance and lag occur. Once a steady state has been reached, the rate of solution reduces because of saturation and other effects. In time, the whole of the coating disappears, so that the loss curve will become concave toward the time axis, and eventually its time derivative will vanish, i.e., it will become parallel to the time axis. It would appear that the graphs in Fig. 5 of Mason and Slunder's paper were not continued to a stage where this last conclusion could be drawn, although the points in Curve 3 of that figure indicate a trend in that direction. It is hoped to revert to this subject at some other opportunity.

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[17] A similar conclusion was drawn previously by Edwards and Keller in reference 8, page 140, on other grounds.

the author is indebted for permission to publish the results. Much is owed to numerous stimulating discussions of the subject matter and observations with Mr. C. A. Bauer, Vice-President of the company, and to Mr. Lester C. Morton for his untiring patience and painstaking care in helping to collect the data. The graphs were kindly traced by Mr. L. Joe Meinert.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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